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Chemical Age

The Chemical Engineer

A Monthly Journal of Practical, Applied and Analytical Chemistry

VOLUME XXIII

January—June 1916

156922
2/11/20.

The Chemical Engineer

608 S. Dearborn Street
CHICAGO, ILL.

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The Chemical Engineer

PUBLISHED MONTHLY

at 608 S. Dearborn Street, Chicago, Illinois

Vol. XXIII.

CHICAGO, JANUARY, 1916.

No. 2.

THE CHEMICAL ENGINEERING OF THE HARDWOOD DISTILLATION INDUSTRY.*

By JAMES R. WITHROW.

It would require more time than we have at our disposal to go into the details of the chemical engineering of the hardwood distillation industry. They will be apparent to a certain extent in the accompanying lantern slides, though many interesting points must not even be mentioned. General features will be pointed out sufficiently to give a broad survey of the problems involved in plant operation.

The industrial demand which the hardwood distillation industry meets is sufficiently indicated by the mere mention of acetic acid, methyl alcohol, acetone, chloroform, and formaldehyde, without burdening you with statistics of their production, consumption, exportation and importation. The number of industries and objectives in the arts which benefit by the availability of these substances is surprisingly great, though not all of them are exclusively the products of this industry.

DEVELOPMENT.

The development of the industry appears to have been very simple. From the earliest times charcoal appears to have been used in the arts and especially in metallurgy. That liquid products could be formed, during the charcoal production, was very early observed. Uses were gradually found for these products and in course of time a demand was created for them with the result that wood carbonization was largely changed in method, so as to improve the yield of the desired by-products.

The historical development of this industry is one of the most interesting in the annals of industrial chemistry, because it illustrates so well the battledore and shuttlecock fortune of so many of these industries. So often the by-product of today becomes the main product of tomorrow; and the new industry, which appears the worst competitive enemy of one industry, becomes the greatest blessing of the old industry in the next decade. The liquid products accompanying charcoal production are said to have been

recovered by the ancient Egyptians and utilized by them in embalming the dead. Pliny mentions their recovery in Syria and Theophrastus in Macedonia.

As chemical knowledge in those days appears to have been very limited and engineering skill as much so, the recovery of liquid products must have been trifling and it was many centuries before chemical knowledge made possible and the arts demanded intelligent development. Notwithstanding the later development of the engineering as well as chemical side of the industry, the essential features of primitive wood carbonization have come down practically unaltered to the present day. This primitive charcoal burning is still practiced wherever wood is plentiful in Russia, Scandinavia, Austria-Hungary, Germany (Westphalia and the Harz), New Jersey, Maryland, etc.

In spite of various uses to which they were put in early times no real appreciation of the value of the liquid substances known to be formed during carbonization of wood came until the dawn of modern chemical investigation. Lack of sufficient fundamental chemical knowledge was largely responsible for this. For instance as early as 1658 Glauber identified the so-called "burnt-wood acid" with acetic acid, yet not until 1802 was it identified with the acetic acid of fermentation, by Thenard. In 1661 Robert Boyle discovered wood-spirit in wood distillate, yet not until 1812 did Taylor notice its analogy to grain alcohol.

The true character of this "spirit" was established only after a series of investigations by Colin, Dobereiner, Gmelin, Liebig, Sweitzer and especially Dumas and Pélégot, ending about 1835. As a result of these investigations together with those on the composition of the wood-tar and wood gas, there came an increased effort to recover such of these by-products as were suitable for use in the arts in general, as well as in the organic chemical industries that were at this time struggling for a footing upon the investigations of the great masters of our science. The first step in this revolution was the use of by-product kilns and retorts, in place of the old sod covered pits or heaps, for carbonization. It would seem that from this point, at least, the development of the industry should have been consistent and perhaps rapid but this was not the case.

*Paper presented at Seattle, Wash., meeting of American Chemical Society.

Apparently the first product to have been systematically recovered was the wood-gas. This was first used in England for illuminating purposes somewhat prior to the chemical developments just mentioned. The honor, however, for the exhaustive investigation of the illuminating, heating and power value of this gas, belongs to the Frenchman, Philip Lebon.

The weakly illuminating wood gas was soon outclassed, however, by the development of coal gas production and the whole hardwood distillation industry had a precarious existence during a large part of the last century even in spite of the fact that a satisfactory method of purifying the crude acetic acid had been devised as early as 1824 by Mollerat and Jasmeyer.

The products of the destructive distillation of coal, such as coke, illuminating gas, tar and tar-distillates were sharp competitors of the wood products. Yet when the wood industry seemed about to be relegated to the primitive woods, the sudden development of the coal-tar color industry started a demand for acetic acid, methyl alcohol and acetone which has since been augmented by the demand for the same products in the production of celluloid and smokeless powder as well as many synthetic organic substances used in pharmacy and the arts. The demand for methyl alcohol within a few years after Perkins' discovery of aniline dyes became so great that the price was enormous. It is not surprising, therefore, that at that time in England wood was distilled with the sole object of getting wood alcohol. A like situation is said to have arisen at one time in benzol manufacture, coal having been for a while distilled with the sole object of obtaining benzol for aniline production.

These general statements regarding the development of the industry bring us to the present situation where we recover mainly the primary products wood gas, raw liquor (pyroligneous acid), tars and oils, and charcoal. It should be noticed in passing that while most engineering skill is a matter of quite recent development and chemical engineering is perhaps the most recently developed phase of engineering, yet it has been able reasonably to keep pace with chemical development in this industry at least, and this may be due largely to the fact that the development of engineering methods and the understanding and fabrication of engineering materials of construction developed along with the science of chemistry and are somewhat dependent upon it.

THE PROBLEM OF THE INDUSTRY.

Broadly speaking, the problem of the hardwood distillation industry is the complete utilization of the weight of the original wood as far as this is possible by economical chemical engineering manipulation, for the production of the products which it will yield of main industrial use or value, *i. e.*, charcoal, acetic acid and methyl alcohol.

Economical chemical engineering involves the use and sequence of such operations as will give the maximum financial return, per unit of raw material con-

sumed, consistent with a proper balance between low cost of operation, low initial cost of plant and highest speed of turn over (processing raw material).

When wood is heated sufficiently in the atmosphere it tends to burn of course to residual ash, steam and carbon dioxide, for the most part. If the air is partially excluded we obtain residual charcoal and volatile products varying widely in composition, depending upon the extent of air exclusion, from the condition of almost complete combustion of volatile products, to practically entire elimination of combustion or atmospheric oxidation when air is excluded as completely as possible.

The problem of the industry may be met therefore by heating the wood sufficiently to carbonize it and in such a way as to eliminate as far as possible any atmospheric oxidation of the volatile products, and at the same time handle the distillates in such a way as to minimize refining or purification difficulties.

Modern chemical engineering skill has met the conditions of reasonably efficient solution of the problem with fair success as is shown by the extent of the industry and without doubt it will advance still further.

Every problem, however large, is merely a series of smaller sub-problems and each of these in turn is often resolvable into still other problems. In studying the problem of any chemical industry it is natural to divide it as far as possible into:

1. The nature of the demand or market for the products, or objectives of the industry.
2. The chemistry involved.
3. The operations or engineering involved.

The chemistry of the hardwood distillation industry finds its basis in the phenomena attending destructive distillation. Much more should be known about destructive distillation than is known. Our concern at this time, however, is with the engineering problems involved in the utilization of this chemistry. Suffice it to say in the matter of the chemistry involved, that the products of heating the wood, as is usually the case in destructive distillation, are gaseous, liquid (condensate) and solid (residual charcoal). The gas as a whole is combustible. The liquid is acid and in two (or three) nearly non-miscible phases—tar (and oil) and dilute alcoholic acetic acid, with dissolved tar and other substances.

CHEMICAL ENGINEERING OPERATIONS.

The engineering operations of the industry group themselves mainly into four divisions as follows:

- I—Preliminary handling of raw material.
- II—Destructive distillation proper or so-called primary distillation.
- III—Treatment of the liquid distillate or secondary distillation.
- IV—Refining operations and derived product production.

The latter is not generally connected with what is known as the Crude Hardwood Industry and will, therefore, be indicated with great brevity.

The engineering operations themselves are as follows:

I—Preliminary Handling of Wood.

- 1—Harvesting the timber—cutting, splitting.
- 2—Seasoning, transportation and storage.

II—Primary Distillation (*Destructive distillation, proper*).

- 1—Loading oven cars.
- 2—Charging and sealing ovens.
- 3—Firing ovens (*Distillation*).
- 4—Condensation and fuel gas recovery.
- 5—Pulling ovens (*Discharging hot charcoal cars*).
- 6—Cooling charcoal.
- 7—Pulling charcoal coolers.
- 8—Ageing charcoal.
- 9—Screening charcoal.

Final Product: Charcoal for the Market.

III—Secondary Distillation (*of condensate obtained in II, 4*).

- 1—Settling "Raw Liquor" (*condensate II, 4*).
- 2—Separation of tar (and oil) from "Raw Liquor" (*continuous decantation*).
- 3—Redistillation of settled tar (*for further recovery of "Raw Liquor"*) from copper or wooden stills.
- 4—Condensation of acid distillate [Oil added to "Boiled Tar," water added to original "Raw Liquor" (*condensate II, 4*)].
- 5—Redistillation of settled "Raw Liquor" (*for further tarry bodies elimination*) from continuous copper stills.
- 6—Condensation of "boiled liquor."
- 7—"Mixing" "boiled liquor" with lime (*Neutralization*).
- 8—Distillation of neutralized "boiled liquor" in lime-lee still (iron).

- 9—Condensation of weak alcohol-acetone.
- 10—Settling or filtering lime-lee still residue (*aqueous calcium acetate*).
- 11—Evaporation and crystallization of lime-lee residues.
- 12—Drying (sacking, weighing, analysis) crystallized acetate of lime.

Product: Grav Acetate of Lime (80 per cent) for the Market.

- 13—Redistillation of weak alcohol-acetone for oil separation and concentration (*Burecy pans, fractionation*).
- 14—Condensation of alcohol-acetone in fractions.

Product: Crude 82 per cent Alcohol-Acetone for Market or Refinery.

IV—Refining and Derived Product Manufacture.

(a) Alcohol:

- 1—Chemical treatment of crude alcohol (NaOH or H_2SO_4).
- 2—Distillation and condensation for elimination of chemicals, etc.
- 3—Fractional distillation in column still.
- 4—Condensation with "heads and tails" elimination.

Product: Refined Methyl Alcohol and Acetone-Alcohol for Market.

(b) Gray Acetate:

- 1—Distillation with sulphuric acid (or HCl).
- 2—Dust elimination from vapors.
- 3—Condensation of acetic acid (*Commercial*).
- 4—Refining by redistillation and fractionation after chemical or electrical treatment.

Product: Refined and Concentrated Acetic Acid for Market.

(c) Gray Acetate:

- 1—Destructive distillation.

- 2—Dust elimination from vapors.
- 3—Condensation of crude acetone and oils.
- 4—Separation of oils from acetone.
- 5—Chemical treatment for acid elimination.
- 6—Redistillation for "white oil" elimination.
- 7—Fractional distillation of acetone.
- 8—Condensation.

Product: Acetone for the Market.

Each and every one of these operations calls for its own special form of apparatus or construction and modifies to a varying extent the design and operation of the plant. They are the essential operations or chemical engineering proper which must be carried out to secure the results obtained in first-class practice. There has been indicated also, in a limited way, how some of these operations must be carried out. Sufficient preliminary discussion of the development of the industry has been given to illustrate the connection which appears to have existed between the development of both chemical knowledge and engineering skill, and the growth and development of this industry.

In concluding I must express my indebtedness to Mr. Edward H. French, to whom I owe my first opportunity (a number of years ago) of working upon the problems of this industry, upon which he has himself engaged, and who has been of much assistance in securing plant photographs from which slides have been prepared.

WHAT CHEMISTRY HAS DONE TO AID THE UTILIZATION OF WOOD.*

By S. F. ACREE.

An attempt to discuss fully the influence of chemistry on the utilization of waste wood leads so deeply into practically all fields of chemistry that a paper of this kind must necessarily be limited to a small number of topics. Attention is given, therefore, to those phases of this subject which are of most importance commercially and which seem to show greatest promise for the future. The number of eminent chemists who have contributed to the few subjects to be discussed is so large that it is impossible to treat their individual researches as they deserve. Such being the case, a brief mention here and there of a few investigations by the Forest Service, with which the writer is personally familiar, will not be understood as a failure to appreciate the work of others.

The technical processes involved in the apparently simple distillation and extraction of woods lead both into the abstruse problems of thermodynamics and into the most refined technique of organic chemistry, and advances in these investigations have been described by Klason, Wislicenus, Klar, Withrow, Palmer, and others. The distillation of waste hardwoods is now one of the most important industries in this country and has reached a high state of efficiency in the

*Paper presented at the Seattle, Wash., meeting of the American Chemical Society.

hands of Messrs. Stevens, Quinn Brothers, Troy, Gaffney, Clawson and the Cleveland Cliffs Chemical Company. There are over 100 plants in operation, in which about 1,200,000 cords of wood are distilled annually.

The chief products obtained are charcoal, acetic acid, methyl alcohol, wood oil, and wood tars, and these are so valuable that extended researches have been made by the Forest Products Laboratory to increase the yields. The quantitative studies on the regulation of the reactions have resulted in improved processes and increased earnings. Charcoal is the least valuable by-product of the wood distillation industry, but is used in large quantities as a household fuel, in decolorizing grain alcohol and other liquids, in the manufacture of gunpowder and lubricants, and in the manufacture of fine charcoal steel. The acetic acid is utilized for the production of such substances as mordants for dyes, acetanilide, and sugar of lead. Acetone is produced by the distillation of calcium acetate and is used to the extent of 3,000,000 gallons annually in the manufacture of denatured alcohol, chloroform, photographic films, celluloid, and, especially, explosives.

Wood alcohol is one of the most striking illustrations which we have today of the value of chemistry and chemical methods in the purification and utilization of a waste product. When Mr. E. B. Stevens, president of the Wood Products Company of Buffalo, N. Y., constructed his first still out of a tin can and attempted to purify the evil-smelling distillate from a near-by wood distillation plant, he little realized what a tremendous future awaited his efforts as an enthusiastic boy of seventeen. Today, crude 82 per cent wood alcohol is changed by simple chemical and physical methods into a product which has a purity of 99.95 per cent. This substance is used all over the world and new fields are being discovered for its utilization. The 10,000,000 gallons produced in this country are used for making celluloid and similar products, dyestuffs, denatured alcohol, photographic films, formaldehyde, artificial leather, varnishes, shellacs, artificial rubber, and other substances too numerous to mention, in whose manufacture and use hundreds of millions of dollars and large numbers of men are employed.

European countries use nearly as much wood alcohol as the United States but chiefly for denaturing ethyl alcohol, for the manufacture of formaldehyde, for the methyl group of aniline colors, and for other purely chemical purposes. There is at present no substitute for wood alcohol in the preparation of the methyl groups of various dyes, especially the violets and blues, and hundreds of millions of dollars are invested in the dyestuff business and in the wool, cotton, linen and silk cloth industries and others using these colors. These dyes are used today in many cases of disease in staining tissues and bacteria, thus allowing medical men to make a proper diagnosis.

Wood alcohol acts as a poison when taken internally, or when its concentrated vapors are inhaled in enclosed spaces, and sometimes produces blindness and death under these conditions. The wood alcohol manufacturers themselves condemn its use as such in any article of food, drink, or medicinal or toilet preparation. When, on the other hand, these objectionable properties are destroyed by chemical changes, it becomes one of the substances necessary for the production of other products for the protection of the health of the community. Pure methyl (wood) alcohol is the only substance which can be converted on a commercial scale into formaldehyde, which is used universally for disinfection against such contagious diseases as smallpox, scarlet fever, diphtheria, tuberculosis, infantile paralysis, and spinal meningitis in its epidemic form. It should, furthermore, be pointed out that many native and alien crop diseases are becoming epidemics in this country and destroying yearly from ten to twenty million dollars worth of foodstuffs, besides infecting the farming lands and rendering them far less valuable for the production of certain crops.

The United States and state governments prescribe formaldehyde as the disinfectant for the seeds, which are sterilized before planting. By this disinfection crop losses, due to certain fungi, can be greatly reduced. Formaldehyde is practically the only efficient disinfectant which can be legally employed in embalming the dead and preventing the spread of contagious diseases causing their deaths. Formaldehyde and phenol are the basis of the manufacture of bakelite which is now used in tremendous quantities in large chemical apparatus in certain industries, and is finding wide use as insulating material in the electrical world. Formaldehyde is, furthermore, used in large quantities in the preparation of various dyes discussed above.

Another by-product from wood distillation, which has received little consideration up to this time, is the hardwood tar. This substance has a large percentage of derivatives which should find wide use in chemical industries. Already we find small quantities of these tars in use as wood tar creosotes for the preservation of wood, and the insufficient production of coal tar creosote in this country will, without doubt, enable wood tar creosote to come into its own, especially as it has been found to have a high toxicity toward certain fungi.

In the field of distillation of softwoods, we find that some of our most important commercial products are obtained by this combination of physical and chemical methods. The chief products are turpentine, pine oils, tar oils, rosin and charcoal. The turpentine is used chiefly in the production of paints, varnishes, and shellac. The pine oils are used to a large extent as solvents and as medicine. The tar oils are used for treating such things as rope and fish nets in order to preserve them in salt water. The rosin is used in

making soaps, paper sizing, varnishes, and shellacs. Charcoal is used chiefly for fuel.

The value of the paper and pulp industry in this country is apparent immediately when we think of the benefit derived from the tremendous number of books, periodicals and of newspapers. Wood pulp is used for making men's summer clothes, papers of all kinds, binder twine to replace sisal, sacks, filter papers and rugs. It is used for making fiber vessels, vulcanized fiber for electrical insulation, and is now the basis of viscose which is finding a wide field of application. Viscose is colloidal cellulose which can be made into "fiber silk" thread and sausage coverings. The thread can be woven alone, or in combination with cotton or silk, into all kinds of fabrics, such as artificial silk socks, neckties, and cloth, all of which can be dyed beautifully in any color. Surgeon's thread, and erasers of this material are cheap and efficient.

Cellulose can be made in a very pure form from certain woods and has been used extensively in explosives. Not only is it converted directly into nitro-cellulose but we find that wood flour is used very extensively as an absorbent in the manufacture of dynamite. The very finely divided wood flour absorbs 60 per cent of nitroglycerine and is more efficient than kieselguhr. This wood flour is also used in making certain grades of linoleum and is much cheaper than cork.

Turning now to the dyestuffs, we find that the aniline industry of Germany has not entirely driven vegetable colors from the market. A number of West Indian and South American woods, such as the fustic, logwood, Brazil wood, and peach wood, are imported into this country and the Forest Products Laboratory has recently been instrumental in calling the attention of manufacturers to the fact that Oklahoma and Texas contain large quantities of osage orange which can be used very cheaply as a source of a valuable yellow dye for textiles and leather. The enormous leather industry is dependent not only upon the use of vegetable dyestuffs but especially upon the tannins obtained from hemlock, oak, chestnut and other materials. Certainly the preparation of tanning material involves the most delicate physical and chemical, as well as biological, operations, as has been shown by the work of Proctor, Stiasny, Levi, Balderston and others.

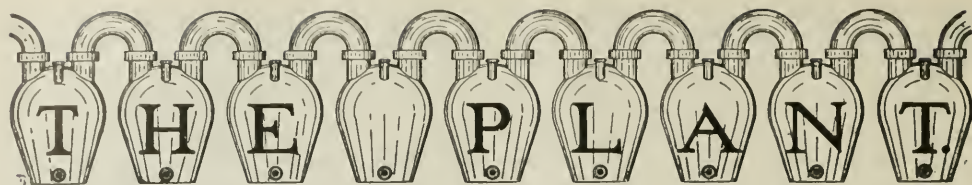
That the production and consumption of ethyl alcohol in the United States is an important activity is emphasized by the fact that the taxes on distilled spirits and fermented liquors amounted in 1913 to \$223,000,000, which was over 65 per cent of the entire internal revenue of the country. It will be recalled that over 100 years ago Braconnot carried out an investigation in which wood was hydrolyzed by acids into glucose, which was then fermented into ethyl alcohol. In recent years, this problem has been studied energetically by Simondson, Classen, Cohoe, Ewen and Tomlinson and others, and four plants were

erected in the United States. Three of these failed but the experience gained thereby and the research work on this problem by the Du Pont de Nemours Powder Company and the Forest Products Laboratory have now made the outlook for this industry very bright. It is believed that a plant could now be constructed under proper conditions of location, transportation, and other such factors, which would make possible the manufacture of ethyl alcohol from sawdust at a price which would allow it to compete with the production of ethyl alcohol from molasses. Especially important in this connection is the discovery by the Forest Products Laboratory that western larch contains about 10 per cent of a galactan yielding only galactose. If fermentation methods can be devised for the commercial conversion of galactose into ethyl alcohol, the western larch butts, which are at present waste material, will become a very cheap source of alcohol. The increased efficiency of alcohol at high pressure in internal combustion engines may thus place this material in a position where it can compete with gasoline when this becomes scarcer.

The preservation of woods in railroad ties, telegraph poles, heavy bridge timbers, structural timbers, and in houses, is one of the most important phases of forest conservation before the public today. In this preservation over 100,000,000 gallons of coal-tar creosote, water-gas-tar creosote, and mixtures of these chemicals with petroleum residues are used. Aqueous solutions of zinc chloride, sodium fluoride, copper sulphate, and many other inorganic chemicals are also used very widely. Millions of dollars are thus involved in an industry whose business it is primarily to preserve this investment. It follows then that chemical methods must be developed for the analysis of the creosotes, and that chemical studies should lead to the manufacture of better materials at lower cost. The Forest Products Laboratory has made investigations on the analysis of creosotes and the isolation of their many constituents, together with tests of the toxicity of these compounds toward wood-destroying fungi, and these researches have shown that great improvements could easily be made in the preservation of wood by the use of better specifications for the materials and methods of treatment.

In the above paragraphs, only a few of the industries involving the utilization of chemical methods in the use of waste wood have been discussed. But daily the problems along these lines are being extended and the future will probably show that the application of chemistry to the utilization of forest products extends into nearly every field of human endeavor.

An extensive aluminum smelter is being established at Høyanger, Norway, where there is a waterfall that may furnish 60,000 HP. A development of 20,000 HP. is proposed, to provide for the production of 4,000 tons of aluminum per year. A capital investment of \$3,350,000 is to be made.



A SUMMARY OF THE EXPERIENCE GAINED IN THE TREATMENT OF THE WASTES FROM THE SCOURING OF WOOL.

By HARRY R. CROHURST† and ARTHUR D. WESTON.††

(Concluded from December issue.)

Table VI gives the analyses of samples of wool scouring liquor from various sources and is taken from Stabler & Pratt's analyses in Water Supply Paper No. 235.

Table VII gives the analyses of wool scouring liquors by Wilson & Calvert in "Trade Waste Waters" from English Mills.

As the discharge from most mills never consists wholly of the concentrated wool scouring wastes, but usually contains the wash waters from the operations of bleaching and dyeing which produce a diluted wool scouring liquor, Table VIII giving analyses is presented to show the difference between the concentrated wool scouring liquor and the composite wastes from the several operations.

A comparison of the analyses in Table VIII with the analyses of the undiluted heavy wool scouring

liquors shows the composite wastes are many times weaker. It might not be out of place to mention in passing, that the first four analyses in Table VIII represent wastes which were experimented upon at the Lawrence Experiment Station to determine the applicability of sewage treatment methods to woolen mill wastes. These wastes were in no way comparable with the heavy undiluted wool scouring liquors. The possibility of treating the wool scouring liquors by sewage methods when diluted with the other mill wastes will be discussed in the author's paper on the treatment of wastes from the finishing processes.

PURIFICATION PROCESSES.

From the foregoing tables of analyses of the wool scouring liquors it will be seen that they are a concentrated, brownish liquor, containing large quantities of organic matter in solution and suspension, soap and alkali used in the process of scouring and a large amount of grease derived from the wool. The waste contains two products—potash and grease—which have considerable commercial value if recovered. Purification processes may consist of those methods used in sewage purification, losing the valuable products contained in the liquor, processes involving partial recovery of valuable products combined with sewage treatment methods, or complete recovery methods. A

TABLE VI.—ANALYSES OF SAMPLES OF WOOL SCOURING LIQUOR FROM VARIOUS SOURCES.

No.	Specific gravity.	Turbidity.	Scum, per cent by volume.	Sediment, per cent by volume.	Solids				Fats.	Oxygen consumed.	Free amm.	Organic nitrogen.
					Total.	Volatile.	Fixed.	Alkalinity.				
Milligrams per Liter.												
1.....	1.023	22,000	15	45,090	24,670	20,120	8,000	14,600	5,680	300	663	
2.....	1.027	120,000	8	116,400	85,000	31,400	8,000	59,000	11,500	300	1,550	
3.....	1.019	55,000	20	68,060	50,710	17,350	3,100	38,200	5,700	164	795	
4.....			20	70,800	46,600	24,200	3,800	31,620	5,200	180	941	
5.....				41,700	29,800	11,900	3,120	20,200				

1. Lymanville Co., Lymanville, R. I., Nov. 13, 1906.

2. Lorraine Manufacturing Co., Pawtucket, R. I. Average 3 samples March 13, 1907.

3. Lorraine Manufacturing Co., Pawtucket, R. I. Average for week ending Mar. 29, 1907.

4. Lorraine Manufacturing Co., Pawtucket, R. I. Average for week ending May 23, 1907.

5. Field Head Mills, Bradford, England. Crude suds, May, 1900.

*Slight.

TABLE VII.—ANALYSES OF WOOL SCOURING LIQUORS FROM ENGLISH MILLS. Parts per Million.

Source.	Total solids.	Nitrogen.		Fats.	Alkalinity.	Potash as K ₂ CO ₃ .
		Ammoniacal.	Organic (Kjeldahl).			
Mixed wools.....	23,883	162	338	8,346	5,433	4,177
Greasy Colonial, home bred, skin wools.....	24,666	91	238	10,189	5,404	3,089
Greasy Colonial Merino wool.....	33,879	196	394	17,995	4,077	
Average of several analyses.....	22,392	115	226	12,378		
Back-washing water.....	8,427	49	87	5,176	415	

discussion of these methods for the treatment of the various classes of waste follows.

PURIFICATION BY SEWAGE METHODS.

Experiments on the purification of wool scouring liquor have for a number of years been in progress at the Lawrence Experiment Station of the Massachusetts State Department of Health under the direction of Mr. H. W. Clark, Chemist of the Department. The

TABLE VIII.—ANALYSES OF MIXED WOOLEN MILL WASTES.

			—Ammonia.—				
			—Albuminoid.—				
Residue on evaporation			In solu-		In sus-		Oxygen
Total.	Loss on	Fixed.	Free.	Total.	tion.	pension.	con- sumed.
1,187	476	711	1	9	..	..	199
1,500	600	900	6	8	3	5	81
2,704	1,215	1,489	4	22	..	..	181
1,623	624	999	1	6	..	..	114
2,744	1,140	1,604	15	27	20	7	230

results of these experiments have been published from time to time in the annual reports of the Department and the following information on the application of sewage methods to the purification of wool scouring liquors is taken from these reports.

Sedimentation.—Plain sedimentation results in the separation of the coarser material, such as sand and mineral matter, washed from the wool in scouring. Only 30 per cent—generally less—of the suspended organic matter can be settled in a reasonable time.

Chemical Precipitation.—All the common precipitants such as lime, ferric sulphate, ferric sulphate and lime, iron alum, alumina sulphate, ferrous sulphate, ferric chloride, calcium chloride, etc., were tried. In all experiments excessive amounts of the precipitants were required to cause any coagulation whatever. Lime up to 30,000 lbs. per 1,000,000 gals. and the same amount of ferric sulphate had little effect, while 50,000 lbs. of sulphate of alumina caused no precipitation beyond coagulation alone. Calcium chloride was the most efficient but 10,000 to 20,000 lbs. per 1,000,000 gals. were required to produce a filtrate nearly odorless. As wool scouring liquor is about 100 to 300 times as strong as domestic sewage, it would be expected that large amounts of precipitant would be required. The fatty matter of the liquor is in a form of emulsion and lighter than water, and the coagulation of this material causes it to rise carrying the coagulating material up with it.

Straining Through Coke.—Considerable clarification can be obtained by treating the waste on beds of coke or cinders. Where the wastes are mixed with domestic sewage, the treatment in settling tanks and on coke strainers, followed by sand filtration, is recommended.

Sand Filtration.—All experiments tried by treating the wool liquor directly on sand beds resulted in the beds clogging and the effluent having the same characteristics as the applied liquor. When clarified by chemicals the liquor filtered readily, but the effluent was similar to the raw waste. When applied to a filter which was treating domestic sewage and when

nitrification was active this was quickly checked by the waste. Combined waste and sewage in the proportion of 1 part waste and 17 parts sewage allowed to rot for 48 hours before filtration gave better results. The results of filtration experiments by the Massachusetts State Department of Health are given in Table IX, p. 374.

From these experiments it seems probable that the treatment of the more concentrated liquors from the scouring of raw wool by sewage methods cannot be recommended as the beds clog rapidly and nitrification will not take place.

Inasmuch as the concentrated waste contains recoverable grease which is the cause of failure of sewage methods, and as the recovery of this grease can at least be made to pay some part of the cost of purification, the best method seems to be the separation of the concentrated liquor, the recovery of both potash and grease or the grease alone, and the purification of the dilute liquors together with the remaining liquors after the recovery process by sewage purification methods.

PURIFICATION BY RECOVERY.

Steeping.—Steeping before scouring is almost unknown in this country, but is practiced in France and Belgium, and to a lesser extent in Germany, Russia and England. It is merely a preliminary step in the scouring process and consists of passing warm water continuously through the wool loosening the impurities and making the later scouring process much easier. The steep water extracts about 40 per cent of the impurities and becomes highly concentrated with potash. This liquor is then evaporated, incinerated and the crude potassium carbonate recovered. The wool is then scoured by the usual method, but the process is much easier as the remaining impurities are softened and can be removed with much less soap and in a shorter time. The soap and alkali added and the grease from the wool contained in this scouring liquor, and their purification involves the same methods that would be used if the steeping process had not been employed.

Volatile Solvents.—At some mills scouring with volatile solvents has been tried but the method is not in general use. In this method the wool is put in suitable containers, is treated with the solvent by continued circulation through it, and finally removed by some inert gas as carbon dioxide. The wool treated in this way can be completely cleansed with warm water. The solvent is distilled and re-used and the wool fat recovered. Such a plant is in operation at the Arlington Mills, Lawrence, Mass. The merits of this process consists in a saving of the wool fiber and a saving in soap in the subsequent washing process. The water used in cleansing after extraction with the solvent is very similar to the steep water in the first process. It contains a greater percentage of wool impurities and is somewhat less valuable for the recovery of potash.

The solvents proposed have been petroleum-naphtha,

at different steps based on 1,000 gals. of scouring liquor at the Lorraine Mills, as shown in Table XI.

The purification accomplished at this plant, based on the following determinations, was as follows: Total solids, 67 per cent; volatile solids, 77 per cent; fixed solids, 46 per cent; fats, 85 per cent.

Turner-Akeroyd Process.—This process is a slight modification of the cracking process, patented in England by Messrs. Turner and Akeroyd, and is employed in the recovery of grease from dilute solutions. The liquor is diluted to such specific gravity that the fats on treatment with acid settle to the bottom leaving a clear supernatant liquor. Such a plant was installed by the firm of Turner & Akeroyd, and operated by them during the year 1906 to 1911 at the Pontoosac Mill in Pittsfield, Mass., to demonstrate the methods of the process. A brief description of this plant follows:

The Pontoosac Mill is located on the Housatonic River about two miles above Pittsfield, Mass. The output consists of woolen cloth. The waste treated

river. The filter for the supernatant liquor has an area of $1/36$ of an acre and consists of 4 ins. of cinders underdrained by broken stone and tile drains also discharging into the river. The hydraulic sludge press has a capacity of 35 to 40 cu. ft. and is provided with steam pipes for treating the sludge in the press.

The operation of this plant is as follows: When a treatment tank is full the compressed air is turned on and a thorough mixing takes place. At this time also about one-third of a barrel of loam is added and from 12 to 15 gals. of sulphuric acid. Mixing then takes place for from 4 to 5 hours and the contents are allowed to settle over night. The supernatant liquor is then drawn off and applied to the filter bed. About 3 to 4 ins. of sawdust are added to the surface of one of the sludge beds and the sludge is applied to the surface. After drying and draining for a day or so the sludge becomes thick and oily and can be removed with a shovel and placed in burlap bags ready for pressing. Any accumulation of grease on the surface of the liquid filter is also treated with this dried sludge.

TABLE XI.—ESTIMATES OF RELATIVE VOLUMES AT DIFFERENT STEPS BASED ON 1,000 GALS. OF SCOURING LIQUOR.

Source.	Total amount of material.		—Water—		Composition			
					Total solids.	Volatile solids.	Fixed solids.	Fats.
	Gals.	Lbs.	Gals.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
Scouring liquor	1,000	8,520	948	7,941	579	406	173	291
Acid used	5.2	77	1.5	13	...	...	...	...
Liquid from acid tanks	620	5,290	619	5,164	126	60	66	30
Filter effluent	225	2,174	254	2,122	52	25	27	12
Material pressed	...	1,093	80	668	425	321	104	249
Liquor from cisterns	167	1,405	167	1,391	14	10	4	3
Liquor from purification of grease....	7	60	7	60	Trace	...	...	Trace
Grease recovered	...	183	...	Trace	183	183	Trace	183
Press cake	...	255	3	27	228	128	101	63
Total liquid effluent	1,049	8,929	1,047	8,737	192	95	97	45

consists of the worst part of the scouring liquors, the wash waters and dye waters being diverted to the river. An analysis of the waste treated is as follows:

Total residue:	
Total	5,224
Suspended	2,048
Loss on ignition:	
Total	3,564
Suspended	1,584
Free ammonia	3.0
Albuminoid ammonia:	
Total	33.0
Suspended	25.8
Oxygen consumed:	
Unfiltered	700
Filtered	515

The purification plant consists of two settling tanks, three sludge beds, a filter and a sludge press, together with the necessary pumps for lifting the liquor, an air compressor and the necessary piping for operating. The settling tanks are each 20 ft. in diameter and 10 ft. deep having a capacity of 20,000 gals. They are provided with inlet troughs, a system of air piping in the bottom for agitation and outlets for the sludge and supernatant liquor. The three sludge beds are each approximately $1/160$ of an acre in area and consist of 3 to 4 ins. of fine cinders underdrained by broken stones and tile underdrains which discharge into the

The bags are treated with steam in the press which liberates the grease and oil which is further purified, barrelled and sold. The dry cake in the presses is used for filling or sold as fertilizer.

Table XII shows the results of a test on the operation of this plant.

The purification, based on the raw liquor and the effluent of the filter, was as follows: Total solids, 60 per cent; volatile solids, 83 per cent; albuminoid ammonia, 91 per cent; oxygen consumed, 94 per cent.

Stable & Pratt give the following analyses of the raw liquor and filter effluent obtained by them from this plant.

	Milligrams per liter.	
	Scouring liquor.	Filter effluent.
Total solids	4,740	2,460
Volatile solids	3,200	100
Fixed solids	1,540	2,360
Free ammonia	2.6	5.6
Organic nitrogen	47.6	6.1
Oxygen consumed	410	64
Fats	2,148	38

The percentage purification based on their analyses was as follows: Total solids, 48 per cent; volatile solids, 97 per cent; oxygen consumed, 84 per cent; fats, 98 per cent.

This plant was operated by the firm of Turner and Akeroyd, and after demonstrating that a profit could be made on the recovery of the grease its operation was discontinued. The owners of the mill believed that while a profit could be made over operating expenses, the profit over operating expenses plus interest on the cost of the plant would be little or none.

The estimated yearly cost of operating such a plant is given as follows:

Labor, 52 weeks at \$12.....\$ 624
Acid 260

Value of oil recovered, say, 3,600 bbls. at \$0.28.....\$ 884
.....\$1,008

Profit\$ 124

Figuring the interest and depreciation on the cost of the works, it will be seen that no profit can be made from the recovery of grease from this class of waste. On the other hand, if the waste was to be treated by sewage methods alone there would be absolutely no return upon the capital expended. When the liquor

mix the contents. Acid is added until cracking occurs and the contents, after thorough mixing, are allowed to settle twelve hours. The supernatant liquor is then drawn off through a floating arm, passed through the settling tank to remove any more fats it may contain and then filtered. The filter beds are four in number, have an area of .023 of an acre, are constructed of cinders 2 ft. deep and are well underdrained.

The sludge from the treatment tanks is treated on eleven filter beds each having an area of 147 sq. ft. About a week's drying puts it in such condition that it can be removed, placed in burlap bags and treated in the presses. Five steam-jacketed hydraulic presses are provided. The grease extracted is pumped to separating tanks and further clarified and barrelled. The sludge remaining after pressing is said to have good fertilizing value and is sold.

The cost of the works was about \$15,000. The cost of operating and returns from the grease extracted are

TABLE XII.—RESULTS OF A TEST ON THE TURNER-AKEROYD PROCESS PLANT AT PONTOSAC MILL, PITTSFIELD, MASS.

Source.	Parts per million.									
	Total residue.		Loss on ignition		Free amm.	Albuminoid ammonia.		Oxygen consumed.		Acidity.
	Total.	Suspended.	Total.	Suspended.		Total.	Suspended.	Unfiltered.	Filtered.	
Wool scouring liquor	5,224	2,048	3,564	1,584	3.0	33.0	25.8	700	515	
Same after addition of acid and 6 hrs. mixing	3,980	2,738	2,560	2,028	3.8	16.0	13.8	240	34	1,025
Supernatant after standing over night	2,312	76	924	64	2.6	3.8	1.6	65	35	
Effluent from filter	2,112	38	596	26	2.6	3.0	0.9	39	34	615
Sludge applied to sludge bed....	22,016	21,722	19,448	18,956	6.0	15.4	14.7	1,350	46	
Effluent of sludge bed	2,482	38	612	32	2.9	2.9	0.2	53	51	690

treated by the cracking process is the heavy concentrated liquor from scouring raw wool the profit from the recovery of grease ought to go far towards paying for the cost of the plant and operating expenses.

Grease Recovery Plant at Hudson Worsted Co.—A plant for the recovery of grease from the scouring of wool has been in operation at the Hudson Worsted Co.'s plant in Hudson, Mass., since 1909. This plant was constructed under the direction of Mr. Robert Spurr Weston, Civil Engineer, Boston, Mass., and has since been operated under his supervision. We are indebted to Mr. Weston for the following notes on this plant.

The works were installed to improve the condition of the river into which the raw waste was formerly discharged and for the purpose of recovering the grease. The cracking process is used and the acid waters are treated by filtration.

The daily wastes, amounting to about 24,000 gals., are collected in a sump from which they are pumped to a cooling trough and then to a settling tank having a capacity of about 15,000 gals. The settled wastes are then pumped to the treatment tanks, of which there are three, each having 20,000 gals. capacity, covered to prevent nuisance from odors. All fumes are carried away from the tanks by exhaust fans and discharged into the stack over the boiler. The treatment tanks are provided with air agitators which thoroughly

not available but it is said that when the grease is sold for 2.5 cts. per pound the plant is run at a loss and when sold for 3.5 cts. at a profit.

So far as is known there are no analyses available of the raw liquor and the effluent of the filters.

Smith-Leach Process.—This method of treatment was in operation in England at the Field Head Mills, Bradford, for several years. It is probably the highest developed recovery process that has been put in operation. Its principle is concentration, separation and subsequent recovery of the potash and wool grease.

The liquor to be treated flows to a preliminary settling tank, which removes the coarser suspended matter, sand and dirt; and then to a Yaryan quadruple-effect evaporator where it is reduced to 1/10 to 1/15 its original volume. The concentrated liquor is then heated nearly to the boiling point and passed through a centrifugal machine which separates it into three portions: an outer layer of sand and dirt, which is removed from the machine by hand, a central layer consisting of soapy liquid which contains potash, and an inner layer of wool grease.

The wool grease is purified by heating with water and then separation takes place, and the potash liquor is further concentrated by evaporation and incinerated until the crude potassium carbonate remains. There is then produced from the raw liquor, distilled water, grease, crude potassium carbonate, mud and sand.

Table XIII from Stabler & Pratt's paper shows the composition and quantity of waste, based on 1,000 gals. of raw liquor, for each step in the Smith-Leach process as conducted at the Field Head Mills:

The above authors give the following balance sheet, as the result of a week's test at the Field Head Plant, made by Chief Inspector H. McLean Wilson of the West Riding Rivers Board:

Cost of plant	\$21,900.00
Amount of wool scoured, lbs.	65,256.00
Amount of scouring liquor, gals.	66,000.00
Value of products:	
3,300 lbs. wool fat	\$ 146.00
2,830 lbs. crude potash	93.98
53,100 gals. distilled water	6.69
Soap saved by using above water, 1/7 total used	10.22
	\$ 256.89
Cost of operation:	
Coal, 19 tons, 41,780 lbs.	\$ 50.54
Labor, 3 men	16.60
Interest and depreciation, 10%	42.10
	\$ 109.24
Profit	\$ 147.65
Profit per year, \$7,677.80=35%.	

During this test the plant was operating at about half its capacity, making the fixed charges relatively high, and during about half the week scoured wool was being washed. The low cost of coal and labor which could not be duplicated here makes the return greater than could be expected from similar plants operating in this country.

Battage Process.—The success of this process depends upon some form of agitator or beater either of compressed air, superheated steam or a mechanical device which will cause a froth or foam to form upon the surface of the liquor. This liquor will contain the fatty material. The foam is removed from the surface by skimming and the grease recovered by treatment with acid and pressing. This recovery process is used successfully in France.

While a portion of the grease is recovered, the process can hardly be called one of purification as the remaining liquor is a very concentrated, dirty waste and

unfit to be discharged into any stream without some additional form of recovery or purification.

Stabler & Pratt give Table XIV, which shows the degree of purification and the profit from the different methods of treating wool scouring liquor.

TABLE XIV.—DEGREE OF PURIFICATION AND THE PROFIT FROM DIFFERENT METHODS OF TREATING WOOL SCOURING LIQUOR.

	per cent purification.			
	Total solids.	Volatile solids.	Fats.	Per cent profit on capital invested.
Cracking process	65	71	83	0
Turner-Akeroyd process:				
Filtration inclusive	48	97	98	0
Filtration exclusive	0	92	92	0
Smith-Leach process	100	100	100	59

SUMMARY AND CONCLUSIONS.

The application of sewage treatment methods to the purification of heavy wool scouring liquor results in failure. Sewage treatment methods for purifying the composite liquors of woolen mills, where washing and dyeing of the finished cloth are practiced and where the heavy scouring liquor is very much diluted, may be applicable; but the process is simply the destruction of a liquor containing valuable products which might by other methods of treatment be made to yield some return on the cost of purification works and their operation.

The common methods of recovery in combination with sewage methods are the so-called cracking process and the Turner-Akeroyd modification. From these methods grease alone is recovered from the waste and considerable revenue can be obtained. The remaining liquid is then treated by filtration and the resulting effluent is well purified. It is doubtful if any profit can be made after paying the fixed charges and operation of the plant. The recovered grease will, however, more than pay the cost of operating the recovery portion of the plant.

TABLE XIII.—COMPOSITION AND QUANTITY OF WASTE, BASED ON 1,000 GALS. OF RAW LIQUOR, FOR EACH STEP IN THE SMITH-LEACH PROCESS.

Source.	Total amount of material.		Water		Composition				
	Gals.	Lbs.	Gals.	Lbs.	Total solids. Lbs.	Grease. Lbs.	Organic im- purities. Lbs.	Soluble mineral matter. Lbs.	Insoluble mineral matter. Lbs.
Crude suds	1,000	8,452	970	8,100	352	174	78	73	27
Concentrated suds	103	959	73	607	352	174	76	63	39
Condensed water	897	7,493	897	7,493	0.5	0.4	0	0.1	0
From concentrated suds:									
Grease	30	125	0.6	5	120	118	0.6	..	1
Potash liquor	73	832	72	601	231	56	55	64	56
Earthy matter	0	2	0	0.5	1.5	0.2	0	0	1.3
	103	959	73	606	352	174	56	64	58
From evaporating potash liquor:									
Crude potash	94	0	0	94	..	2	64	28	28
Loss	738	72	601	137	56	53	0	28	28
		892	72	601	231	56	55	64	56

By the Smith-Leach process the wool scouring liquor can be entirely destroyed, the resulting products being grease, potash, distilled water, sand and mud. No liquid remains to be treated by sewage methods. From such data as are available, this method of disposal will yield a fair return upon the cost of the plant and cost of operation, and there remains no liquid of a polluting nature to cause nuisance.

ELECTRIC STEEL DIRECT FROM ORE FINES.*

By A. C. DALTON.

In a recent paper the statement was made: "The electric furnace will have realized its highest attainment when it is employed directly for making pig steel from iron ore. Already this has been demonstrated as a possibility in Sweden." It will be of interest to many to know that the same possibility is being demonstrated on the American continent, along somewhat new lines, which promise to be equally successful.

I described in *The Iron Age* of Oct. 15, 1914, the Moffat electric furnace at the Moffat-Irving Steel Works, Ltd., Toronto, Canada, for treating fine ores, without subjecting them to any mechanical treatment other than concentration, briquetting or sintering. The process was then described in detail with the results of some experiments on flue dust. The flue dust was

the fuel and flux being all showered in some 13 ft. above the level of the bath.

In the treatment of the fine materials by such a process as this the question naturally arises: Is there not a high mechanical loss due to the fines being carried up the stack by the ascending gases? While no direct method has yet been employed to estimate this, the quantity that so escapes is practically negligible under normal conditions. This is accounted for by the fact that no forced air is put into the furnace; only natural draft is used. This is further substantiated by the high percentage of recovery it is possible to obtain under good conditions, as shown in Table 1, when heat K gave 97.1 per cent total recovery of the iron charged.

The practice in detail is much the same as described for the flue dust experiments in the article referred

TABLE II.—ANALYSIS OF THE PIG STEEL.

Heat.	Combined Carbon, Per Cent.	Silicon, Per Cent.	Sulphur, Per Cent.	Phosphorus, Per Cent.	Manganese, Per Cent.
A	0.12	0.06	0.121	0.015	0.08
B	0.06	0.03	0.07	0.017	0.07
C	0.70	0.02	0.054	0.013	0.13
D	0.06	0.04	0.085	0.015	0.01
E	0.06	0.04	0.119	0.019	0.02
F	0.05	0.05	0.088	0.016	0.02
G	1.18	0.06	0.109	0.012	0.06
H	0.10	0.02	0.062	0.009	Trace
I	0.06	0.03	0.073	0.007	0.02
J	0.04	0.06	0.086	0.005	Trace
K	1.36	0.04	0.151	0.018	0.18

TABLE I.—DETAILS OF THE CHARGES OF THE HEATS WITH CONSUMPTION OF ELECTRICITY.

Heat.	Duration of Heat.		Ore.	Coal.	Lime.	Recovery, Per cent.	Kw. Hr. Per Lb. of Metal in Ore.
	Hr.	Min.					
A	2	50	1,000	150	65	68.00	1.015
B	4	15	1,600	270	100	70.00	1.34
C	2	25	1,000	250	200	44.20	1.02
D	3	55	1,000	280	210	72.60	1.70
E	3	40	1,000	200	75	...	1.47
F	4	30	1,000	280	210	67.50	1.14
G	4	00	1,600	350	210	88.20	1.23
H	3	00	850	152	150	85.80	1.25
I	3	10	1,000	188	184	90.40	1.27
J	3	05	1,000	200	175	84.50	1.32
K	3	35	1,000	275	200	97.10	1.36

from hematite practice and was easily reducible, but as the results were very promising, much interest was naturally shown as to what success would be met with in the treatment of the more refractory iron ores.

SMELTING MOOSE MOUNTAIN MAGNETITES.

A suitable opportunity occurred for a series of trial runs with the Moose Mountain magnetites. The results are of considerable metallurgical interest. The figures here given are only of an experimental nature and with the exception of heats D, E and F are from intermittent runs. Local circumstances prevented continuous runs, which would have improved considerably many of the figures in Table 1. It is also necessary to remember that in this process there is no solid body of materials in the furnace, the ore along with

to, the chief alteration being that anthracite coal screenings have been substituted for the coke breeze for these reasons: The lower sulphur content of the coal and better reduction with anthracite. The other alteration was the replacing of limestone for lime, because this allowed of much better feeding control.

Owing to the fact that much of the Moose Mountain magnetite is so intimately banded with silicious materials, the ore has to be crushed to a considerable degree of fineness for concentration purposes, the concentrates for these experiments being exceptionally

TABLE III.—ANALYSIS OF THE SLAGS.

Heat.	SiO ₂ , Per Cent.	FeO, Per Cent.	Al ₂ O ₃ , Per Cent.	CaO, Per Cent.	MgO, Per Cent.
A	17.52	33.94	13.16	19.21	...
B	20.04	19.31	5.36	19.66	5.25
C	30.12	14.90	9.40	27.19	...
D	20.80	27.77	9.97	15.18	26.24
E	23.60	19.58	9.84	21.84	21.14
F	19.20	46.11	5.13	11.46	15.04
G	34.90	10.93	12.33	35.29	8.90
H	28.40	18.21	5.65	30.45	...
I	17.20	50.09	7.03	19.18	...
J	22.00	40.54	5.31	24.42	...
K	34.20	8.67	11.50	36.81	...

fine, 200 mesh. The figures for the electricity consumption are the high tension readings and they therefore include all transformer losses, etc., which are normally 10 per cent and this should be clearly understood. In the tables will be found the analyses of the materials used and of the pig steel produced as well as slags. Table 1 gives the details of the charge with the electricity consumption in k.w. hr. per pound of metal in the ore charged.

*From *The Iron Age*.

METALLURGICAL POSSIBILITIES.

The more important phases of the process are the metallurgical possibility and the uniform control of the product. It is now generally accepted that the final deoxidation of iron ores is done by the solid carbon. It was necessary therefore in this process to keep the fuel of sufficient coarseness and excess so that some of the carbon should reach the bath in the solid form. Further experiments were made where the proportion of carbon was considerably increased and decreased, and it is interesting to notice the effect of this procedure in the percentage of carbon in the steel and the increase of the FeO in the slag. These figures tend to confirm the experience of other investigators that the lower the carbon content of the pig steel, the higher will be the ferrous oxide in the slag.

There is danger in having too large an excess of carbon as was pointed out by Professor Richards some time ago, when he said: "That in electric melting one danger was an excess of carbon. Since no air is blown into the furnace any excess above that consumed in the reduction must remain unused, accumulate and eventually clog the furnace." He then advocated the use of a tuyere to deliver excess air as this would always be responsible for a given amount of carbon. It would not be advisable, however, to introduce air under pressure in this process, but the same result was obtained with complete satisfaction using natural draft. As the furnace allows observations of the bath to be frequently taken it is easy to regulate the amount of carbon feed if any undue excess occurs.

In the treatment of fines by such a process there will always be a higher percentage of FeO in the slags

TABLE IV.—ANALYSIS OF RAW MATERIALS.

Moose Mountain Concentrates.	Limestone.	Coal Screenings.
SiO ₂ 8.20	SiO ₂ 0.98	Ash 17.40
FeO 23.01	FeO Al ₂ O ₃ .. 0.29	Sulphur 0.75
Fe ₂ O ₃ 65.68	S. Trace	F. Carbon... 72.10
Al ₂ O ₃ 2.19	P. Trace	Vol. Matter. 10.00
CaO Trace	CaCO ₃ 97.69	
MgO 0.10	MgCO ₃ 1.36	
SO ₂ Trace		
P ₂ O ₅ 0.49		
TiO ₂ Trace		

owing to the ore being in such a finely divided nature. This of course will be somewhat modified with perfect control of the slag which will be one of greater difficulty than in ordinary reduction furnaces. This control of the slag is finely balanced with the physical conditions and unless the two are working in correct proportions erratic results will be obtained. Heat E is an example where this occurs. The coal charged was considerably less yet the carbon remained practically the same as in heats D and F. The deficiency of lime is clearly seen in the rapid rise of the sulphur in the steel. A thin, hot, fluid slag of course is the secret of the process and fortunately the furnace allows of such variation in its feeding device that almost instant effect can be produced on the bath.

UNIFORMITY OF THE STEELS.

In spite of this it is interesting to see how comparatively uniform are the analyses of the steels produced, where no attempt at uniformity was made except in heats D, E and F. These three heats were run consecutively and it is noticeable that the electricity falls as the furnace gets hotter. The high consumption in the first heat was due to a thick heavy slag caused by the action on the furnace bottom. The recovery is not as good as would have been expected, but was due in this case to some of the metal not being poured owing to the action on the furnace bottom. In other cases the low recovery is explained by the fact that a lot of the fines were adhering to the walls of the hearth and were partially reduced. This, in continuous running, would obviously be lessened.

Sufficient has been done with these preliminary runs to satisfactorily demonstrate the metallurgical possibilities of such a process in the treatment of ore fines. Owing to these experiments being of an intermittent nature, it is inadvisable to publish any data as to the costs, but there is sufficient reason to believe that the final costs will be within commercial limits and some further experiments of a more extensive nature are about to be undertaken, with a view to establishing the commercial standing of the process. Any such data should necessarily be held until the results of this future work are completed.

The results obtained by this process at present show that such refractory ores as magnetites in an extremely fine state of division can be smelted without first being subjected to any other treatment than concentration and that there will be no difficulty in producing a high grade pig steel of uniform composition.

MANUFACTURE OF SILICA BRICK FOR THE BY-PRODUCT COKE OVEN.*

By KENNETH SEAVER.

In no operation has the employment of silica brick spread with such leaps and bounds as in the carbonization of coal, particularly in the by-product coke oven. Today, in practically all types of oven, the structure above the floor level (except the facings) is of silica, while in the recuperative and in some regenerative types, its use is extended below the oven floor as well.

Because there are a number of refractories of higher silica content than the usual so-called fire-clay brick, there is sometimes a confusion as to what is meant by "silica" brick; we here refer only to a brick having a silica content of 94 per cent or more, made usually from the quartzite rock with a small percentage of lime as a binder.

The term "silica" brick is sometimes rather loosely applied to brick made from highly siliceous clays, or

*From paper presented at San Francisco meeting, American Institute of Mining Engineers.

to a quartzite refractory of mingled fire-clay and quartz rock; but such products are not considered in this discussion.

MATERIALS.

The rock from which practically all high-grade silica brick are made is a true quartzite or metamorphosed sandstone, variously known as ganister, quartz, quartzite, silica rock, etc.—the largest fields, in the order of their relative importance being those of Pennsylvania, Wisconsin, Alabama and Colorado.

Pennsylvania manufactures from 75 to 85 per cent of the silica brick made in the United States; nearly all from the quartzite found in the Medina and Oneida formation, quarried in Huntingdon and Blair counties. In this restricted area the quartzite is at its best; toward the north and south it becomes softer, is no longer a true quartzite, or is too much impregnated with iron. The rock is easily accessible in the counties mentioned, enormous quantities lying loose on the surface along the Juniata River and its tributaries.

In the course of time it has been weathered and broken up into loose rock or "flocs," as they are called, which may cover an area of a thousand acres or more. The depth usually varies from three or four to as much as 20 ft. Smaller flocs formed in the same way are found along the flanks of the mountains; but they nowhere compare in size with those formed where the measures have been cut transversely.

This rock is sometimes quarried out of the solid measures, but by far the largest quantity used is that taken from the bodies of loose rock as the latter is not only cheaper to work but is of more uniform quality. The white Medina formation is not composed entirely of quartzite, but is made up principally of sandstone with intermingled strata of quartzite. Thus, where the formation has been broken up, the softer sandstones unsuitable for the manufacture of silica brick have weathered away and disintegrated, leaving the larger part of the flocs consisting of quartzite. When sandstone is mixed with the quartzite in the flocs it is readily detected by its appearance, as it becomes much more rounded and worn in weather than the quartzite, which retains its sharp angular edges.

The individual pieces in these flocs range from fist-size to boulders weighing many tons. Probably 50 per cent of the rock occurs in pieces weighing more than 500 lbs. The largest flocs are found at the gorges of the Juniata River near the towns of Mount Union, Mapleton, Point View, Lewistown, etc.

It is interesting to note that the Oriskany sandstone, extensively used as glass sand, is found in close proximity to the Medina, and that although exceedingly pure in its composition, its softness renders it unsuitable for high silica brick. It consists of a mass of minute quartz grains, loosely held together, and often so friable that it can be easily worn away by the hands. On the other hand, the Medina quartzite consists of quartz crystals cemented in a mixture of the same

composition. The difference in the two types of rock, when ground for the manufacture of brick, is obvious. The harder stone gives splintery, angular fragments; the other, rounded grains. Experience shows that a hard rock like the Medina is required for physically strong silica brick.

A representative analysis of the Pennsylvania quartzite is as follows:

	Per Cent.
Silica (SiO_2)	97.80
Alumina (Al_2O_3)	0.90
Ferric oxide (Fe_2O_3)	0.85
Lime (CaO)	0.10
Magnesia (MgO)	0.15
Alkalies	0.20
	100.00

METHOD OF MANUFACTURE.

Grinding.—After the rock, broken to one man size, is received at the brick plant, it is put through a crusher, which reduces it to practically the size of a 1 in. to 2 in. ring. It is then elevated to storage bins, from which it may be fed in weighed quantities to the wet pans for grinding.

Into the wet pans, as the grinding proceeds, 2 per cent of lime, by weight, is introduced as milk of lime, which, when the brick is burned, serves in combination with the other elements, to give the necessary bond or physical strength.

The fineness of the grinding depends upon the nature of the brick to be made. In general, one charge, containing material for 200 bricks, will be ground, at the rate of approximately four pans per hour for standard 9-in. brick, while to obtain the fineness requisite for the intricate and difficult shape-work necessary in by-product coke oven construction, but two pans per hour may be possible. The rock is exceedingly hard, and a comparatively slight increase in the fineness of grind is accompanied by a seemingly disproportionate lowering of grinding capacity, and increased wear on the pans.

The difference in the ground rock lies, not so much in the actual size of either the coarse or fine grains, as in the relative proportion of fines. There can be no question that the general effect of increasing the fineness of grind is to improve the abrasive resistance of the brick, and the requirements for typical coke oven specifications have worked no hardship upon the manufacturer; for the present-day standard of workmanship on oven shapes is such as to "carry its own grind with it," if the expression may be used. To secure the accurate filling out of shapes, and the clean-cut accuracy essential, the grind is actually much finer than is necessary to satisfy the usual specifications as to that feature.

Molding.—The ground silica material when ready to mold is of about the consistency of damp sand, but probably because of the extreme angularity of its grains has less flow as it is manipulated. As a consequence, the molds must be filled by pounding with heavy plank beaters, and all corners and shapes of

irregular outline must be rammed by hand, much as sand molds are made, but with much heavier blows. Unequal ramming, which leaves a variation in the density of the green brick, will give unequal expansion in the kiln. It is by no means uncommon to lose hundreds of a difficult shape through such fire-cracking. To get proper molding and ramming requires the strictest supervision.

The wear on the steel molds is exceptionally severe, and they are often decidedly complicated, and always expensive, as "loose sides" must be used. The molded silica has almost no strength, and can be taken from the mold only by allowing the sides to come with it, after which the sides are stripped.

After molding, the shapes are placed on pallets and dried, either on a steam heated hot floor or on rack cars in some form of tunnel dryer. The brick are then ready to be set in the kilns.

Burning.—The majority of silica brick are burned with soft coal in the familiar type of round, down-draft kiln. The following schedule of burning may be considered as fairly normal. When the setting is complete and the doors are sealed, fire is immediately started, and continued slowly with slight acceleration for 9 to 12 days, during the last 2 or 3 of which the final temperature should be practically attained. The kiln is then held at the required temperature, say at 26 cone (1,650° C., or 3,002° F.) directly in front of the firebox, for another day; after which the fireboxes may be sealed, and allowed to remain thus for approximately 24 hours more. Cooling requires about as long as the burning.

Effect of Burning on Composition and Expansion.—In discussing the desirable qualities of silica brick it is frequently said that "all the expansion shall be burned out of them." This brings out the questions: What is the nature of this expansion; what produces it; what is its extent, and how fully can it be controlled?

Let it be premised that all silica brick are made in molds smaller than the proposed finished or burned brick; and that under the influence of heat a permanent expansion occurs, swelling the brick from the mold or "green" size to the required or "burned" size. It is desirable that this permanent expansion be completed during burning so as to preclude further permanent expansion when in use.

Expansion will occur on heating—a true thermal temporary expansion that will disappear upon cooling; which must not be confused with the permanent expansion produced in the brick during the manufacture. If a silica brick is not properly burned, then, upon reheating in actual coke-oven use, there will be not only its normal thermal expansion, but an additional permanent expansion. It is essential in the construction of the coke ovens that the expansion, whatever its

nature, be as small as possible, and that, whatever it is to be, it be known and adequately cared for.

It will be recalled that the silica brick under consideration is formed by adding 2 per cent of lime to quartzite rock of the following composition, say:

	Per Cent.
Silica (SiO_2)	97.80
Alumina (Al_2O_3)	0.90
Ferric oxide (Fe_2O_3)	0.85
Lime (CaO)	0.10
Magnesia (MgO)	0.15
Alkalies	0.40
	100.20

The representative silica brick produced may be assumed to have the following composition:

	Per Cent.
Silica (SiO_2)	96.25
Alumina (Al_2O_3)	0.88
Ferric oxide (Fe_2O_3)	0.79
Lime (CaO)	1.80
Magnesia (MgO)	0.14
Alkalies	0.39
	100.25

What are the changes which occur as the siliceous mass is burned?

Certain of them are obvious; such as the formation of a bond of one or more of the lime-silica compounds such as the meta-silicate CaO , SiO_2 or 2CaO , SiO_2 . With the exception of the lime present, the ferric oxide and the alumina though small in quantity are the preponderating impurities, and there is undoubtedly formed a certain amount of silicate of iron as well as compounds of the lime-alumina series. Whereas the lowest melting point incident to any eutectic of the lime-silica system is 1,436° C. (2,617° F.) and of the alumina-silica series is 1,610° C. (2,930° F.), while that of the lime-alumina system is 1,400° C. (2,552° F.), some of the eutectics of the ternary system CaO , Al_2O_3 , SiO_2 melt at approximately 1,170° C. (2,138° F.) and are thus among the first of the flux compounds resulting.

No less important, though less recognized, changes occur in the brick as it is heated. The evidence of this change, is seen by the most casual measurement when brick are drawn from the kiln from time to time, as higher temperatures are reached. The final expansion will be very close to $\frac{3}{8}$ in. per foot. The theory of this expansion is that a change occurs in the crystalline form of the silica, an inversion from the quartz crystal to the crystalline form of cristobalite.

It must be borne in mind, that by quick burning, the brick may be easily expanded by double or treble the normal amount; but sound brick do not result. This excessive expansion is due to minute fissures opened up in the body of the brick by a sudden rise in temperature during burning. In the early stages of firing the heat must be raised very slowly.

PRELIMINARY EXPERIMENTS ON THE EFFECT OF TEMPERATURE CONTROL ON THE YIELD OF PRODUCTS IN THE DESTRUCTIVE DISTILLATION OF HARD-WOOD.*

By R. C. PALMER,†

It is well known that in the destructive distillation of wood the products methyl alcohol and acetic acid are formed by a decomposition of the wood substance and that the reaction is accompanied by an evolution of heat. The heat supplied by the exothermic character of the decomposition when added to the heat furnished from some external source, tends to raise the temperature at which the reaction is taking place. Increasing the temperature of the wood beyond the point where spontaneous decomposition takes place will increase the speed or violence of the reaction, and this condition in turn will accelerate the rate at which the temperature is further increased.

There can be no doubt that subjecting the methyl alcohol and acetic acid to an excessive temperature

1. By causing the reaction to take place at as low a temperature as possible.

2. By decreasing the speed of the reaction.

These two methods may be in effect the same under certain circumstances, owing to the exothermic nature of the reaction, since low temperature distillation is a result of slowing down the reaction.

The fact that increasing the time of distillation will increase the yield of valuable products is generally known in commercial wood distillation practice. Lengthening the time of the complete process simply means slowing down the entire decomposition. In the study described in this paper, the application of temperature control to the critical stage of the decomposition has shown that a similar result may be obtained without increasing the time.¹

EXPERIMENTAL.

In making a large number of destructive distillations² in laboratory apparatus as a part of studies on the relative value of different species of hardwoods, it became apparent that the temperature at which the reaction took place and the critical stage had as much

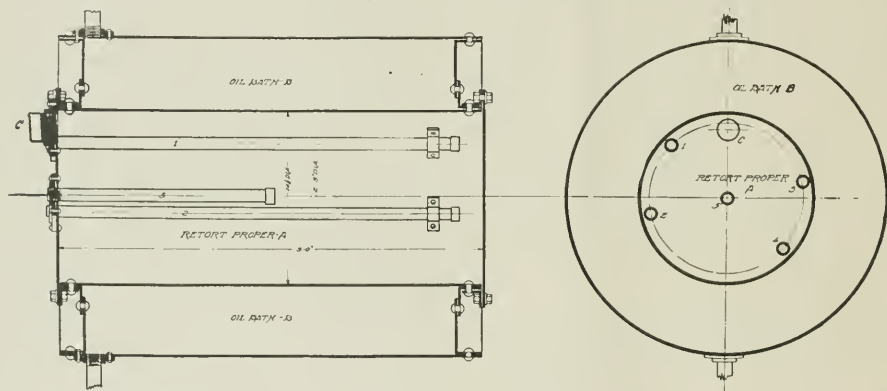


Fig. 1.—Experimental Laboratory Retort.

at the moment of formation may result either in an immediate decomposition of some of these products or may prevent their formation from some intermediate products, and probably increases the tendency for many secondary reactions to take place.

Several facts would seem to fully substantiate this viewpoint. The yield of alcohol and acid in the destructive distillation of wood is much less than the proportion of methoxy and acetyl groupings would lead one to expect. Small scale distillations, where the opportunity for secondary decomposition and interactions are minimized by better control, frequently yield much more acid or alcohol than the usual commercial distillations.

These fundamental considerations indicate that the speed and temperature of the destructive distillation reaction have an important effect on the formation of alcohol and acid. It would seem then that the amount of these products could be materially increased:

influence on the yield of products as the theoretical considerations would indicate.

A more detailed laboratory study of this interpretation of temperature control was therefore made. The basic principles developed were then applied to a commercial plant in order to determine their practicability. The experiments were carried on at the Forest Products Laboratory,³ Madison, Wis., and in the plant of the Cleveland Cliffs Chemical Company, Gladstone, Mich., as a part of a series of studies on methods of increasing the yields of valuable products in the destructive distillation of hardwoods.

This opportunity is taken to acknowledge the assistance and many helpful suggestions of Mr. H. C.

¹Attention was first called to the effect of "slow and fast" distillation on the yield of products by Sennft, but since the comparison was made between distillation from the cold and distillation beginning with red hot retorts, the results could not be interpreted to actual practice.

²A detailed description of methods of distilling the wood and analysis of products is given in United States Department of Agriculture, Bull. 129, "Yields from the Destructive Distillation of Certain Hardwoods."

³Maintained by the Forest Service, U. S. Department of Agriculture, in co-operation with the University of Wisconsin.

*From The Journal of Industrial and Engineering Chemistry.
†Chemist in Forest Products, Forest Products Laboratory, Madison Wisconsin.

Merriam, operating superintendent in the wood distillation plant of the Cleveland Cliffs Iron Company, in conducting the commercial experiment and interpreting and applying the results.

PART I—LABORATORY DISTILLATION.

Apparatus.—The retort used in the laboratory studies is shown in Fig. 1. This retort (A) held approximately 80 lbs. of wood. The oil jacket (B) completely surrounded the circumference of the retort, the ends being insulated with heavy asbestos packing. The oil was heated by means of a row of 20 Bunsen burners, the flame playing largely on the side of the oil jacket, as in this way it was found that a fairly good natural circulation of the hot oil could be obtained. By means of the Bunsen burners the temperature of the heating medium was controlled fairly easily.

The temperature within the retort was measured in three places: At (1) which is close to the inner shell of the retort, directly above the point where the flames play on the oil jacket; the temperature at this point was also approximately the highest temperature of the oil at all times; at (4) which is a point at the bottom of the retort near the inner shell corresponding to (1); and at (5), the center of the retort.

Uncontrolled Distillation.—The laboratory retort distillations were made in all cases on pieces of wood approximately 18 in. $\times$ 2½ in. $\times$ 1 in. sawed from 1 in. lumber to insure average material. The raw material consisted of maple, beech, and birch. The largest number of tests were made with maple and the best comparisons obtained with this species. The samples tested in comparative runs did not differ more than 2 or 3 per cent in moisture content, and showed from 12 to 15 per cent of the dry weight as moisture.

For the purposes of studying the effect of control it was necessary to have for comparison distillations conducted rapidly and at a comparatively high temperature. The manner of making the distillations was as follows: The burners were so regulated that the maximum temperature of the oil was not higher than 270° C. until the center of the retort reached at least 175° C., at which point it was considered that the moisture in the charge was largely distilled off. As soon as the center temperature was about 175°, the gas was so regulated that the oil was raised as quickly as possible to about 350° C. in the distillation allowed to proceed to the end. The distillation practically stopped when the center reached its maximum temperature and began to fall. In all cases this maximum in the center was higher than the temperature of the oil (indicated at (1)) showing the exothermic character of the reaction. The exothermic reaction was further indicated by a rise of 30 to 50° C. in the center after the gas was turned off and the

temperature at (1) was falling.

A distillation of this kind was comparable in many ways with the commercial method of distilling, especially in relation to the rise in temperature during the critical part of the distillation.

The exothermic destructive distillation of hardwood begins at approximately 275° C. and this point is indicated by the appearance of free tar in the distillate. In the laboratory, where the temperature difference between the heating medium and the wood is negligible and the variation in temperature in different parts of the retort is not great, the critical part of the distillation may be considered either as the period after the average temperature has reached 275° or after tar appears in the distillate.

Controlled Distillation.—The control of the distillation, as interpreted in this study, required that the largest possible portion of the reaction be completed at the lowest possible temperature, or, in other words, that the rate of rise of temperature during the critical state of the reaction should be at its minimum. The control distillations were conducted by regulating the burners so that the heating medium was not higher than the critical decomposition temperature (275 to 300° C.) until the temperature in the retort and the rate of flow of distillate indicated that the reaction was being stopped. The center temperature indicated at (5), (Fig. 1) usually passed 275° C. and reached nearly 300° C. when the temperature in (1) began to fall, indicating the checking of the reaction. The oil bath was then raised as quickly as possible to 350° C. and the distillation allowed to finish.

The crude pyroligneous acid liquor obtained in the distillations was analyzed for its acetic acid and alcohol content by the methods given in "Technologie der Holzverholung," by M. Klar, p. 337.

RESULTS OF LABORATORY TESTS.

The results of the laboratory tests are given in

TABLE I.—RESULTS OF LABORATORY TESTS ON EFFECT OF TEMPERATURE CONTROL ON YIELDS OF DISTILLATION PRODUCTS.

Species of Wood Used.	Yield of Wood Alcohol.			Yield of Acetic Acid.		
	Uncontrolled.	Controlled.		Uncontrolled.	Controlled.	
	% of wt. of dry wood.	% of wt. of dry wood.	% of wt. of dry wood.	Lbs. 80% acetate of lime per cord.	% of wt. of dry wood.	Lbs. 80% acetate of lime per cord.
Maple	1.54	2.16	10.2	5.29	2.40	6.80
	1.59	2.36	11.15	5.74	267	5.45
	1.62	2.41	11.25	5.91	275	5.52
Av.	1.59	2.31	10.90	5.65	261½	5.56
Beech	2.01	2.15	9.80	5.70	259	6.28
	2.03	2.15	9.80	5.78	262	6.28
	2.07	2.15	9.80	5.85	266	6.28
Av.	2.04	2.15	9.80	5.77	262	6.28
Birch	1.59	1.73	7.6	6.58	284	6.96
	1.67	1.76	7.7	6.50	281	6.78
Av.	1.63	1.75	7.65	6.54	282	6.87

*The average yield from a number of more normal uncontrolled laboratory distillations on maple was 9.00 gallons of alcohol and 253 pounds of acetate.

†In converting the acetic acid yields to acetate of lime, the results have been decreased 5 per cent in order to allow for the usual commercial sludge loss.

⁴The oil used was a high flash cylinder oil, f. p. 350° C. The temperature was raised above this point by keeping the oil under 15 to 20 pounds pressure, the pressure being relieved only when the decomposition became excessive as indicated by a rapid rise in pressure.

Table 1. The data are given (1) in terms of percentage of wood alcohol and acetic acid per unit weight of the oven-dry wood distilled and (2) as gallons of 95 per cent alcohol and lbs. of 80 per cent acetate of lime per cord of wood. One cord is taken as 80 cu. ft. of solid wood based on actual determination of a commercial cord which equaled 3,425 lbs. for maple wood containing 15 per cent of its dry weight as moisture.

From these data the effect of controlling the distillation is seen to increase the yield of alcohol 45 per cent for maple, 6 per cent for beech, and 7 per cent for birch, while the increase in acetic acid was 2, 9, and 5 per cent, respectively.

Interpretation of Results.—The curves designated X in Fig. 2 show the relation between the percentage

off during a rise in temperature of 22° while at a corresponding period in curve B the rise was 33°.

The uncontrolled runs given for maple were pushed as fast as possible in order to give a reaction that would determine the extreme effect of this procedure as compared with especially controlled methods. A number of more normal uncontrolled distillations for this species gave 9.00 gal. of alcohol per cord and 253 lbs. of acetate. The curve is not shown for these runs; it lies very nearly between A and B but with a slope more like curve B.

Similar curves for the distillations on beech and birch have not been shown, but these were found to lie much closer together than the curves for maple and have only slight differences in rate of distillation (upward slope of curve). It may, therefore, be con-

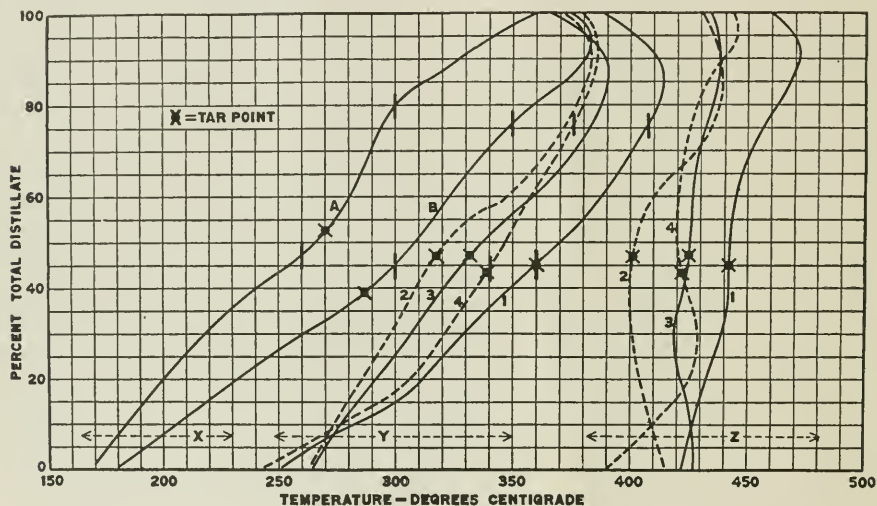


Fig. 2.—Relation between Temperature and Distillate.

X = Laboratory Retort Vapors. Y = Commercial Retort Vapors. Z = Commercial Retort Vapors.

of total distillate and the average temperature of the retort (average of the temperatures indicated at (1) and (5), Fig. 1). Curve A is the average for the controlled distillations and curve B the average for the uncontrolled distillations obtained with maple wood. The tar point has been indicated on each curve and the portion of the curve above the tar point, principally that nearest to it, is considered the critical stage of the distillation.

From curves A and B it would appear that two things might account for the marked increase in alcohol:

1. The actual temperature at which the reaction has taken place in curve A is from 20 to 50° C. lower than curve B.

2. The rate at which the distillation has taken place, indicated by the per cent distillate per degree rise, is slower for A than for B. The first 20 per cent of distillate after the tar point in curve A came

sidered that the comparatively small increases in yields for these species are explained by relatively less actual control of the distillation as compared to the runs with maple.

In the case of the maple runs the yields of alcohol obtained in the laboratory tests, particularly those obtained in the more normal uncontrolled distillations, are very nearly the same as yields from commercial plants, but the yields of acetate are about 40 per cent higher than commercial yields. It will be noted that the small average increase in acetate in the controlled runs is due to an exceptional run while the yields from the other two are actually lower than two of the uncontrolled runs. Neither varying the temperature of the reaction within the limits of the laboratory test nor a change in the rate of distillation appears then to be the cause of the high acetate yield. However, it was known that the temperature at which the distillation reaction is carried out commercially is much

higher than in the laboratory and an application of this fact seemed to be a possible method of approaching the laboratory yield.

In order to test the practical value of these results, it was, of course, necessary next to conduct distillations with a commercial retort. The commercial test was made (1) to measure the yields of alcohol and acetate produced by approaching the laboratory temperature during the critical stage, especially since the commercial acetate yield was so much lower than the laboratory results; (2) to determine if the increase in yield of alcohol produced by a control of the speed of the exothermic reaction could be duplicated on a large scale; and (3) to determine the economic application of any results obtained.

PART II—COMMERCIAL DISTILLATION.

Apparatus.—A diagrammatic sketch of a commercial retort and setting similar to the one used in the test is shown in Fig. 3. The retort held two cars, each having a capacity of $2\frac{1}{4}$ cords, or a total of $4\frac{1}{2}$ cords of wood. The retort was fired at two points on one side and the hot gases passed along the bottom of the retort in opposite directions, up the sides and ends before passing up the stack. A and B were pyrometers placed in the top flue gases and the average temperature at these points was taken as the average temperature of the heat being applied to the retort. The pyrometer C was located in the center of the outlet pipe as close to the retort as the outer brick casing would permit and its readings were assumed to be the average temperature to which the distillation vapors had been subjected in the retort.

The retort was fired with soft coal and at certain periods with the uncondensable gases coming from some other retort. The experimental retort was one of a battery of ten, five of which supplied fuel gas to the other five during about 7 out of 24 hours.

Manipulation.—The experiments were made while the entire plant was in usual operation and in order to determine the yields from the single retort the distillate was caught in 50-gal. barrels. The distillate was thoroughly mixed in the barrels and samples of equal volume taken from each. The mixed sample, therefore, represented an average of the entire distillate. This sample was analyzed⁵ for alcohol and acetate by commercial methods of determining the yields of products in this manner.

The total amount of wood for each charge was weighed and the relative amount of each species determined and moisture samples taken.

At the outset it was of course evident that the practical value of the test depended on introducing no procedure that would reduce the efficiency of operation. Since an increase in the time of distilling seemed the most likely drawback, it was decided to vary the method of firing or change the manner of distillation only so as to insure that the run would be

finished in the usual cycle of 24 hours. Without exception the retort was "pulled" at the end of that time.

The raw material consisted of 93 per cent maple, 4 per cent birch, and 3 per cent beech, as an average. It was in all cases 4-ft. cord wood ranging from 6 to 8 in. in maximum diameter. From 35 to 45 per cent of the dry weight of the wood was water, which was 10 to 20 per cent more moisture than the average distillation wood contains. In view of the necessity of adhering to the 24-hour cycle, the high moisture content materially shortened the time available for temperature control.

Distillation.—Observations of the temperatures produced by the usual method of firing were first made and the yields determined for comparative purposes.

With the apparent effect of the temperature of distillation as an explanation of the high yields of acetate in the laboratory, experiments were first made in which the critical distillation point was brought as nearly as possible to the laboratory temperature.

In the commercial test, where the heating medium is necessarily at a much higher temperature than that desired in the retort because of the large diameter to be penetrated, the critical stage could not be observed, except by the indication of tar in the distillate. All distillations were, of course, made from a hot retort, the previous charge being "pulled" within two hours at most after finishing.

It was at once apparent that the temperature was

TABLE II—RESULTS OF COMMERCIAL TESTS TO DETERMINE THE EFFECT OF TEMPERATURE CONTROL ON THE YIELDS OF DISTILLATION PRODUCTS.

OF DISTILLATION PRODUCTS.									
Group No.	As used for tests.	Lbs. wood per cord.		% of wt. of dry wood.	Gal. 95% alc. per cord.	% of wt. of dry wood.	Lbs. of 80% acetate ² of lime per cord.	% of wt. of dry wood.	Charcoal. Lbs. per cord (20 lbs. to bu.)
		Free from moisture.	% moisture ¹ based on dry weight.						
1	4265*	3025	41.0	1.70	8.2	3.75	187	36.4	53.5*
	4250	3025	40.6	1.99	9.56	4.05	201	34.2	51.75
	4120	3010	36.9	2.01	9.63	3.92	194	35.5	53.5
	4075	2910	40.0	2.09	9.67	4.03	188	34.7	50
	Av.	4160	2982	39.2	2.03	9.62	4.03	194.5	34.8
3	4050*	2965	36.5	2.06	9.73	4.36	213	36.5	54.25
	4070*	2970	37.2	2.07	9.8	4.34	212	37.6	54.75
	4325	3000	44.4	2.16	10.32	4.15	205	37.2	56.25
	4060	2965	36.9	2.11	9.95	4.24	207	36.0	53.5
	Av.	4125	2975	38.75	2.10	9.93	4.25	209	36.9
4	4175*	3060	39.2	2.18	10.42	4.24	209	37.8	56.5
	4040	3025	33.5	2.25	10.78	4.39	218	34.4	52
	4175	3000	39.2	2.27	10.80	4.33	214	37.4	56
	3860 ³	2805	37.7	2.30	10.27	4.45	205	34.7	49
	Av.	4130	3008	37.3	2.23	10.66	4.32	213.6	36.4

¹The moisture content of runs * were not determined, but were estimated from runs with corresponding weights per cord that were determined.

²The acetate included 15 pounds per cord obtained from the settled tar by distillation.

³This run was not included in the average for this group, as the charge consisted of very badly decayed wood, also shown in the light weight per cord. The curves for this run were the same as the average for the group. The yields in per cent of dry wood are seen to be the highest of any run, but the light weight per cord brought down the yields on the cord basis.

⁵Estimated from a number of commercial distillations.

⁵The methods of analysis were the same as those used in the laboratory tests.

not the important factor since the laboratory yields were not approached.

In attempting to carry the distillation within the low temperature range of the laboratory retort, it was found that the critical stage of the distillation proceeded very rapidly for a while, but had to be pushed hard at the end, in order to complete the run in 24 hours.

A series of runs was then made in which the method of firing was varied in several ways, in order to produce differences in the temperature at which the exothermic reaction took place and also the rate of distillation during the critical state.

RESULTS OF COMMERCIAL TESTS.

The results of the different distillations on the commercial retort are given in Table II. The different runs were not made consecutively, but have been divided into groups including similar tests.

The results are given both in percentage of the unit

raised continually until the destructive distillation point is indicated by the flow of distillate and the appearance of tar. The fire is then held steady for a while and then pushed at the end to "make charcoal." It should be noted especially that curve Y1 is very close to the general slope of B—the uncontrolled laboratory distillation.

Group 2.—In this group is shown the effect of bringing the distillation temperature as low as possible for as long a time as the cycle would allow. In curve Y2 it is seen that the distillation reaction went very rapidly after the tar point was indicated. These runs have been designated as "slow drying—fast exothermic." In all cases the rise in temperature is due partly to the exothermic heat and partly to the external fire but in this group much of the rapid sloping off of the curve is due to the exothermic reaction. In distillations of this kind the bottom of the retort became so hot that in practice this procedure would be imprac-

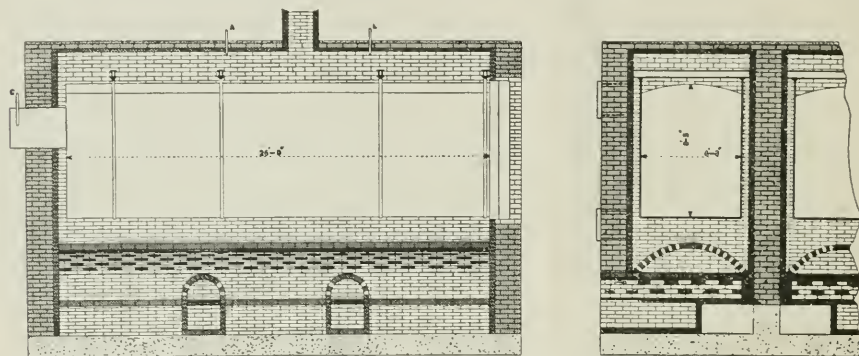


Fig. 3.—Experimental Commercial Retort.

weight of dry wood and in the commercial units, gal. of 95 per cent wood alcohol and lbs. of 80 per cent acetate of lime per cord.

Interpretation of Results.—The results have been interpreted as in the laboratory tests by drawing the curve showing the relation between the percentage of total distillate and the temperature. These curves are shown in Fig. 2 for comparison with the laboratory tests. The curves are numbered to correspond with the groups and are the average of all the runs in that group. The curves designated Y show the relation between the distillate and the temperature of the vapors (indicated by the pyrometer C, Fig. 3) while the curves Z show the relation between the distillate and the heat applied to the retort (indicated by the pyrometers A and B, Fig. 3) for the corresponding groups. The results for the different groups are summarized in Table III.

Group 1.—This is the usual commercial method of firing and has been described as "fast drying—fast exothermic reaction."⁶ The method of firing to produce this kind of distillation is clearly indicated in Fig. 2, curve Z1. The temperature of the retort is

tical for continuous operation because of excessive depreciation.

Curve Z2 shows the manner of firing. It should be

TABLE III.—SUMMARY OF EFFECT OF TEMPERATURE CONTROL ON THE YIELD OF PRODUCTS.

	Wood alcohol.		Acetate.		Charcoal.
	Gals. 95% per cord.	Increase over uncontrolled runs.	Lbs. 80% per cord.	Increase over uncontrolled runs.	Bushels per cord.
Laboratory uncontrolled...	7.50		261		
Laboratory controlled....	10.90	45	266	2	
Commercial Group 1—Fast drying, fast exothermic...	8.2		187		53.5
Commercial Group 2—Slow drying, fast exothermic...	9.62	17.3	194.5	4	51.75
Commercial Group 3—Fast-drying, slower exothermic than Group 2.....	9.93	21.1	209	11.8	55.4
Commercial Group 4—Fast drying, slow exothermic.	10.66	30	213.6	14.2	54.8

⁶Most of the curves Y up to the tar point simply indicate the removal of moisture from the charge. The moisture content of the different groups was as follows: (1), 41 per cent; (2), 39.2 per cent; (3), 38.75 per cent; (4), 37.3 per cent. These are close enough together to make the curves entirely comparable. An analysis of the distillate up to the tar point was made for one run in Group 3 and indicated 21.9 per cent of the total alcohol and 28.7 per cent of the total acetate obtained in the run.

pointed out that the cold wood in the hot retort at the start takes up a large amount of heat and while the temperature of the fire was actually being lowered the normal quantity of fuel was consumed.

Compared with Group 1, the method of distillation showed an appreciable increase in alcohol and acid.

Group 3.—This group is really a modification of Group 2 and is, therefore, described as "faster drying—slower exothermic reaction than Group 2." This is clearly seen in curve Y₃. Curve Z₃ shows that the retort was fired by allowing the temperature to fall slightly during the first part of the drying stage and then keeping the fire on a gradual rise until the last few hours when the temperature was increased more rapidly in order to insure good charcoal.

A decided increase in yields over Group 2 is shown. In the light of the laboratory curves, this increase must be attributed to the slower exothermic reaction rather than the effect of temperature.

Group 4.—The results obtained by the method of distilling used for this group prove conclusively the importance of the rate of distillation on the yields of alcohol and acid, since the highest yields are obtained in these runs. As shown by the curves, these runs were made by "fast drying and slow exothermic reaction."

Referring to curve Z₄, it is seen that the drying period was accomplished by a rapid rise in temperature (or steady firing), and in this stage the distillation curve Y₄ parallels curve Y₁ very closely.

The important procedure in achieving this manner of distillation was the anticipation of the tar point as indicated in the bending back of the Z curve before the tar appeared. In practice, if the distillate can be observed as it flows from the end of the condenser, the time to lower the temperature of the fire would be noted by the first appearance of particles of tar, which precedes the true tar point by from one to two hours. When wood of a uniform moisture content was being used, this method might, however, be replaced by firing at a definite time period.

A comparison of curve Y₄ with curve A of the laboratory-controlled runs indicates the similarity of the slopes of these curves, especially after the tar point.

Fuel.—The fuel required in the different groups is given in Table IV.

TABLE IV—FUEL USED IN COMMERCIAL TEST PER CORD OF WOOD DISTILLED.

Group No.	Coal. Pounds.	Gas. Hours.	Total fuel as coal. Pounds.
1.....	240	10	412
2.....	352	4	412
3.....	250	10	407
4.....	275	12	463

Owing to the variation in the length of time gas was used, the results, as actually measured, are not comparable. On the basis of one run made without gas, which required 412 lbs. of coal per cord, compared with Group 1, in which 240 lbs. of coal and 10

"hrs." of gas were used, 1 hr. of gas was taken as equivalent to 15 lbs. of coal per cord. Then on calculating the "hrs." of gas into coal for the different groups, the results are shown in the last column of Table IV under "total fuel as coal." On this basis, Group 4, which gives the highest yields of alcohol and acetate, would require the equivalent of about 50 lbs. more coal per cord. This would be practically negligible where waste wood was used as fuel, but with coal at \$3.50 per ton it would amount to about 10 cents per cord additional fuel cost.

COMMERCIAL APPLICATION.

In the commercial application of temperature control as developed in this preliminary study, an accurate method of measuring temperature would be required, and probably for successful operation also the employment of a head fireman. Economically the balance is apparently drawn between the cost of installing pyrometers, the employ of a day and night head fireman for at least each 50 cords per day distilled, and the additional small fuel cost per cord, as compared with a possible increase in yield of 25 lbs. of acetate and 2½ gals. of alcohol per cord. Also the control distillations were shown to be possible within the time required for the usual cycle of operation.

CONCLUSIONS.

It was shown in the small scale distillations that a lowering of the temperature of the process and decreasing the speed with which it took place gave marked increases in the yields of alcohol. Also the laboratory methods gave much higher yields of acetic acid than those obtained commercially but this yield was not greatly affected by varying the laboratory methods.

It is now seen in applying these variations in methods of distilling on a much larger scale that a change in the rate of distillation produces practically the same results on the yield of alcohol while the actual temperature of the reaction is not shown to be of as great importance. If it could be shown that the formation of alcohol in the destructive distillation reaction and its probable secondary decomposition into methane and carbon monoxide in the presence of the hot charcoal is reversible, the increase in alcohol by control of the reaction, allowing an accumulation of the end products, would be easily explained.

If the products after formation are lost by decomposition, the greater stability of alcohol after formation as compared to acetic acid seems evident since the large retort which probably involves many interreactions gives practically the same yields of alcohol as the small apparatus while the acid yield is much less than the laboratory yield.

Any process of approaching the high laboratory production of acetic acid will probably have to involve some method of preventing the interreactions in the large apparatus.

It is not improbable that still higher yields than those given can be obtained in the commercial plant

with the application of temperature control alone. Thoroughly air-seasoned wood would require appreciably less time to enter into the destructive distillation stage, thus giving a better opportunity to lengthen the period of slow reaction. The drying stage would also not require so high a temperature at the end, thus bringing all but the last portion of the reaction into a lower range of temperature.

These tests are considered as a preliminary indication of the results that may be obtained from this interpretation of temperature control. The study of this phase is being continued by longer runs comprising an entire plant. Other phases of directing the destructive distillation reaction of wood to produce maximum yields of products are also being made by the United States Forest Products Laboratory.

SUMMARY.

I.—Destructive distillations of hardwood in the laboratory on 70-lb. samples indicated that lowering the temperature of the reaction and decreasing the speed of the distillation at the critical stage increased the yield of methyl alcohol 45 per cent.

II.—The laboratory distillations gave 40 per cent more acetate of lime than commercial yields, but the acetic acid was not greatly influenced by variations in the method of distilling.

III.—The application of the laboratory methods to a commercial retort holding $4\frac{1}{2}$ cords of wood indicated possible yields of alcohol 30 per cent higher than by the usual methods of firing and an increase of 15 per cent in yields of acetate of lime.

IV.—The best results were obtained by slow distillation during the critical stage rather than by lowering the temperature at which the reaction took place. This was accomplished by rapidly removing the moisture content of the wood in the first stages, and then anticipating the period when destructive distillation or critical stage began. At this point the temperature of the fire was decreased.

V.—This method of temperature control gave promise of being entirely applicable in the commercial plant. The fuel requirements were only slightly higher than the usual methods of firing and the cycle of operation was not changed.

VI.—The studies of temperature control have shown that wood alcohol either exhibits sufficient stability in the retort or its formation is of a simple enough character to allow it to be easily effected and the amount recovered greatly increased. Acetic acid, however, is apparently much more subject to variations in the original wood decomposition and methods of preventing the many interreactions going on in the complex vapors of a large retort will be required to secure yields of this product that will more nearly approach the theoretically possible yields.

POTASH FROM THE SEAWEED OF THE SARAGOSSA.*

The current shortage of potash compounds has assumed most serious dimensions. The ordinary commercial chloride of potash (80 per cent muriate of potash) is now quoted at \$600 per ton. The rate in July, 1914, was \$38.

Attention has been directed to the possibility of exploiting deposits of seaweed which are present in such abundance in the so-called Saragossa Sea of the Central Atlantic. Vast amounts of this seaweed are thrown upon the coasts of the Bahamas. In one harbor, the accumulations of hundreds of thousands of tons render at times navigation almost impossible.

The dried kelp obtained from this seaweed contains on an average 9 per cent of potash. In a recent communication by Consul W. F. Doty, of Nassau, it is suggested that efforts should be made on a large scale to exploit this source of potash. Concessions might be obtained for operations on the Bahama Islands, or the work could be carried on directly in the Atlantic.

Although this source of potash-bearing material lies so near to the seaports of the Southern Atlantic States, where such large amounts of potash are currently required as fertilizer, it would appear doubtful whether the proposition offers any advantage over the utilization of the kelp on our Pacific littoral.

KELP FROM PACIFIC COAST CONTAINS MORE POTASH.

As shown in the recent report issued by the United States Bureau of Foreign and Domestic Commerce on "Potash production in California and potash from kelp," the dried kelp from the Pacific coast contains 18.9 per cent of potash. The nitrogen content is also far higher than that of the seaweed in the waters of the Atlantic.

The desirability of securing potash at any price whatever is now so marked that it might possibly be well to consider the question of undertaking an exploitation of the Saragossa weed.

Full data concerning this seaweed can be obtained from the Marine Biological Bureau of the Carnegie Institute at Washington. A prominent fertilizer company in Georgia has also instituted investigations in this connection and it plans to send an expedition to the Bahamas for further exploration.

In the meantime the efforts to perfect and expand the production of potash from the kelp of the California coast are being advanced on a scale of increasing importance. There is but little doubt that, in harmony with the suggestions contained in the recent studies on this subject published in *Commerce Reports*, the California production will be enormously augmented in the early future. There is great hope that it may prove of the most pronounced value in relieving the potash famine at present so much felt in the tobacco and cotton fields of the South.

*From Daily Commerce Reports.



REPORT OF THE COMMITTEE ON RESEARCH AND ANALYTICAL METHODS, DIVISION OF FERTILIZER CHEMISTS, AMERICAN CHEMICAL SOCIETY, NEW ORLEANS, APRIL 2, 1915.

PHOSPHATE ROCK.

The following tentative standard methods for sampling and determination of moisture, phosphoric acid and iron and alumina in phosphate rock are recommended to the division:

Methods of Sampling and Determination of Moisture.

I. Gross Samples.

(a) Car shipments—100 pounds sample per car.

1. Sampling from the car.

In sampling car shipments in the car at least ten scoopshovelful, aggregating 100 pounds, shall be taken from each car at approximately equal distances from each other so as to average the car. Care shall be taken to see that each scoopful shall cover the entire face of the pile from floor to top.

2. Sampling from the cart or barrow.

A small hand scoopful of one or two pounds shall be taken from each cart or barrow either as it is being loaded or as it leaves the car.

(b) Cargo shipments—100-pound minimum sample per vessel.

1. Sampling. In hoisting tub.

In sampling cargoes generally running from 1,000 tons upward a small hand scoopful shall be taken from approximately every tenth tub before it is hoisted from the hold.

2. Sampling from conveyor.

If unloading is being done with automatic bucket and conveyor, periodical sections of the entire discharge of the conveyor shall be taken at such intervals and in such quantities as to give a sample equivalent to approximately one pound per each ten tons of cargo.

3. Sampling from conveying vehicle.

Samples shall be taken with a hand scoop from various cars at such regular intervals and in such quantities as to give approximately one pound for each ten tons of cargo.

II. Laboratory Sample.

The resulting gross sample obtained by any one of the methods outlined shall be crushed to four mesh, thoroughly mixed on a clean, hard surface, and quartered down to a 10-pound average sample.

(a) **Crushing.**

This 10-pound sample shall all be crushed to pass an eight-mesh screen.

(b) **Mixing and quartering.**

This eight-mesh sample shall be carefully mixed and quartered down to two two and one-half pound samples.

(c) **Grinding.**

1. Moisture sample.

One of these two and one-half pound samples shall be held in an air-tight container. This sample is to be used for the determination of moisture.

2. Analytical sample.

The other two and one-half pound sample shall be further mixed and quartered to a two or four-ounce sample, which is then to be ground to 60 mesh. This sample is to be used for the analytical determinations.

Note:—It is essential that the taking of the gross sample be done with small hand scoops, and that the practice of taking the sample in the hand be absolutely prohibited, for it has been found that there is considerable selective action in the finer materials sifting through the fingers, while a scoop retains the entire sample.

The dimensions of the screens referred to above are as follows:

No. of Mesh.	Size of Opening.	Diameter of Wire.
	Inches.	Inches.
4	0.185	0.065
8	0.093	0.032

III. Determination of Moisture:

Moisture is to be determined on both the moisture sample and analytical sample. Of the moisture sample not less than 100 grams are to be weighed out. Of the analytical sample approximately two grams are to be weighed out. Both are to be dried to constant weight at a temperature of 105° C. in a well ventilated oven.

IV. Calculation of Results:

The percentages of phosphoric acid and iron and alumina as determined on the analytical sample are to be calculated to a moisture-free basis and subsequently to the basis of the original sample as shown by the moisture content of the moisture sample.

Determination of Phosphoric Acid.

Reagents: To be prepared as in official methods, A. O. A. C. Bureau of Chemistry, Bulletin 107 (rev.) 1910, P. 2. Preparation of reagents, (c), (d), (e) and (f), except that the ammonium nitrate solution in (d) is changed to 5 per cent instead of 10 per cent.

Method of solution: To 5 grams of the sample add 30 cc. of concentrated hydrochloric acid (sp. gr. 1.20) and 10 cc. of concentrated nitric acid (sp. gr. 1.42) and boil down to a syrupy consistency. The residue, which should be nearly solid after cooling, is taken up with 5 cc. of concentrated nitric acid and 50 cc. of

water. Heat to boiling, cool, filter and make up to 500 cc. through the filter. This procedure eliminates practically all of the silica, and it is necessary to filter as quickly as possible after digestion so as to avoid redissolving the silica.

Determination: Draw off an aliquot portion of 50 cc. corresponding to 0.5 gram, neutralize with ammonia and just clear with nitric acid. Add 15 grams of ammonium nitrate (free from phosphates), heat the solution to 50° C. and add 150 cc. of molybdate solution. Digest at 50° C. for fifteen minutes with frequent stirring. Filter off the supernatant liquid and test the filtrate with molybdate solution to see if precipitation has been complete. (If not, add more molybdate to the filtrate and digest for fifteen minutes longer.) Wash with 5 per cent ammonium nitrate solution by decantation, retaining as much of the precipitate as possible in the beaker. Dissolve the precipitate in the beaker in the least possible quantity of ammonium hydroxide (sp. gr. 0.90) and dilute this solution with several times its volume of hot water. Dissolve the remainder of the precipitate on the filter with this solution, washing beaker and filter with hot water and keeping the volume of the filtrate between 75 and 100 cc. Neutralize with hydrochloric acid, cool to room temperature and add 25 cc. of magnesia mixture from a burette, drop by drop, stirring vigorously with a rubber-tipped rod, then add 15 cc. of ammonium hydroxide (sp. gr. 0.90) and allow to stand for four hours or over night at room temperature. The time of standing may be reduced to two hours if kept in a refrigerator or, still better, in an ice water bath. Filter through a platinum or porcelain Gooch crucible, fitted with a carefully made asbestos or platinum mat and ignited to constant weight. Wash with 2.5 per cent ammonium hydroxide until practically free from chlorides, dry, ignite, cool and weigh as magnesium pyrophosphate. If desired, filtration may be made through an ashless filter paper, igniting in the usual manner. Calculate to P_2O_5 by multiplying by 0.6378 (log 80468).

Determination of Iron and Aluminum Together as Phosphates.

1. Solutions required.

(a) Hydrochloric acid (1:1), prepared by mixing 1 part by volume of concentrated HCl (sp. gr. 1.2) with 1 part of distilled water.

(b) Saturated solution of ammonium chlorid, which should be filtered before use.

(c) 25 per cent solution of ammonium acetate, faintly acid to litmus paper.

(d) Solution of ammonium phosphate (10 per cent), prepared by dissolving 20 g. of $(NH_4)_2HPO_4$ in 180 c.c. of distilled water and filtering. (This should be prepared frequently in small quantity, as it attacks glass containers on standing.)

(e) Standard solution of ferrous ammonium sulphate, containing iron equivalent to about .0100 g. of Fe_2O_3 in 10 c.c. and 50 c.c. of conc. HCl per liter.

(f) Solution of calcium and magnesium phosphates for blank determinations, prepared as follows: Dissolve 4 g. of MgO and 35 g. of $CaCO_3$ (both free of iron and aluminum) in 100 c.c. of conc. HCl. Add an aqueous solution of 30 g. of $(NH_4)_2HPO_4$, make up to 2 liters and filter.

(g) Solution of ammonium nitrate (5 per cent) for washing precipitates. About 400 c.c. are required for each determination.

All reagents used should be as pure as practicable and all solutions should be free of suspended matter.

2. Preparation of rock solution.

Place 2.5 g. of pulverized rock with 50 c.c. of 1:1 HCl in a graduated 250 c.c. flask, the glass of which contains less than one per cent of iron and alumina oxides.¹ Boil gently with occasional shaking for one hour in such a manner as to avoid concentrating the solution to less than half of its original volume²; dilute, cool to room temperature, make up to volume and mix; filter immediately through a dry filter into a dry flask, discarding the first few c.c. of the filtered solution.

Pipette a 50 c.c. aliquot, representing 0.5 g. of rock, into a platinum dish and evaporate nearly to dryness.³ Cool, take up with a few c.c. of water, and when the salts are loosened from the dish, add 5 c.c. of 1:1 sulphuric acid and evaporate to fumes. Increase the temperature and evaporate nearly to dryness.⁴ Cool, dilute with about 50 c.c. of distilled water, add 10 c.c. of conc. HCl and heat with occasional stirring until sulphates are dissolved. Filter into a 600 c.c. Jena glass beaker through a 9 cm. paper (S. & S. No. 597), washing the paper thoroughly with dilute HCl and hot water.

4. First precipitation with ammonium acetate.

To the solution in the beaker add 25 c.c. of the standard iron solution when the amount of combined iron and aluminum oxides in the rock does not exceed 5 per cent and 50 c.c. of the standard iron solution when the combined oxides exceed 5 per cent.⁵ Oxidize with about 3 c.c. of bromin water and boil in covered beaker for about 15 minutes to expel the excess of bromin. Rinse cover and sides of beaker with distilled water and cool to room temperature.

(Run a blank determination containing 10 c.c. of 1:1 HCl, 25 c.c. of the calcium and magnesium phos-

¹Experiments have shown that the solution cannot be made in flasks of glass containing a higher percentage of alumina, because the fluorin in the rock partially dissolves the glass and adds alumina to the solution. Neither "Nonsol," "Jena," nor "Weher's" resistant glass "R" is suitable. Flasks made of glass containing little alumina, such as "Kavalier," "F Z Resistant glass" or other Bohemian glass of lower alumina content, have proven satisfactory. See Chemical Glassware, P. H. Walker, Journal American Chemical Society, Volume 27, 865.

²This may be accomplished by heating the flask over a low Bunsen flame or on a hot plate which is just hot enough to keep the solution boiling. A glass tube about 12 inches long by $\frac{1}{2}$ of an inch in diameter with a bulb in the middle makes a very satisfactory condenser when placed in the neck of the flask.

³It is advisable to remove as much of the HCl as possible before adding sulphuric acid so as to minimize the chances of loss by effervescence or bumping. The evaporation may be conducted in glass beakers of low alumina content. Kavalier has been used satisfactorily. In no case should the evaporation be conducted in porcelain.

⁴It is best to remove as much sulphuric acid as possible so that the calcium sulphate which might hold iron will dissolve readily in HCl.

phate solution, and the same quantity of standard iron solution as is added to the rock solution.)

Add 100 c.c. of saturated ammonium chlorid solution,⁶ 3 c.c. of 10 per cent ammonium phosphate solution, 2 drops of methyl orange indicator and conc. ammonium hydrate (free of spangles and dissolved mineral matter) to alkaline reaction. Then add dilute HCl (about 1:20) drop by drop with constant stirring until the solution becomes faintly acid and the pink color of the methyl orange is just restored.⁷ Dilute to 450 c.c.⁸ with distilled water, heat to boiling, and add 25 c.c. of 25 per cent ammonium acetate solution. Continue heating for about 5 minutes, after adding ammonium acetate, filter on a 1½ cm. ashless filter paper (S. & S. No. 589 "White Ribbon" is suitable) in a 3-inch rapid filtering funnel, keeping the contents of the beaker and funnel hot.⁹ Wash three times with hot 5 per cent ammonium nitrate solution, each time cutting the precipitate loose from the filter and stirring it thoroughly with the stream from the wash bottle and filling filter to within about ¼ inch of its upper edge. About 30 c.c. are required for each washing. Return the precipitate to the precipitating beaker by washing it out of the filter with a stream of hot water. Dissolve the precipitate with dilute HCl (1:6), pouring about 50 c.c. through the filter in successive washings and using about 25 c.c. to wash down inside the beaker. Finish washing filter paper with distilled water.

5. Second precipitation with ammonium acetate.

Cool the solution to room temperature, add 50 c.c. saturated ammonium chlorid solution, 4 c.c. of 10 per cent ammonium phosphate solution, 2 drops of methyl orange, and adjust acidity as before. Dilute to 300 c.c. with distilled water. Heat to boiling, add 15 c.c. of 25 per cent ammonium acetate solution and continue heating for about 5 minutes. Filter on the same paper as used for the first filtration, scrubbing the inside of the beaker with a rubber-tipped stirring rod and rinsing with hot 5 per cent ammonium nitrate solution. Wash the precipitate 10 times with hot 5 per cent ammonium nitrate solution, each time cutting the precipitate loose and stirring it thoroughly as before and breaking up all lumps that it may contain. About 500 c.c. of wash solution are required.

As a precautionary measure, boil the filtrate and washings from both the first and second precipitates, and recover any additional precipitate.

6. Ignition of precipitate.

Transfer filter with precipitate to a weighed deep-

form porcelain crucible (40 mm. in diameter is a good size) and heat gently over a low flame until the contents are dry; increase the temperature a little and continue heating until the paper is charred, increase the temperature again and continue heating until the paper is entirely burned. Ignite the uncovered¹⁰ porcelain crucible for one hour periods over blast lamp or No. 4 Meker burner to constant weight, each time cooling to room temperature in desiccator before weighing. Deduct the weight of blank from each determination, and after subtracting the weight of FePO₄ equivalent to the amount of iron found in 0.5 g. of rock by titration, calculate the remainder to Al₂O₃. $AlPO_4 \times 0.4184 = Al_2O_3$.

DETERMINATION OF IRON.

1. Solutions Required.

(a) Standard potassium permanganate, N/40, containing .79015 g. of KMnO₄ per liter, and having a value of .001096 (or practically .002) g. of Fe₂O₃ per c.c. Standardize with pure sodium oxalate. (Bureau of Standards standard sample No. 40.)

(b) Stannous chlorid. Dissolve 50 g. of the crystallized salt in 100 c.c. of hot conc. HCl and make up to 1 liter with distilled water.

(c) Mercuric chlorid. Prepare a cold, saturated solution.

(d) Manganese solution. (Preventive solution) (A) dissolve 200 g. of crystallized manganese sulphate in 1,000 c.c. of water. (B) Pour slowly, with constant stirring, 40 c.c. of conc. sulphuric acid into 600 c.c. of water and add 1,000 c.c. of phosphoric acid of 1.3 sp. gr.

Mix solutions (A) and (B).

2. Analytical procedure.

Determine iron according to Jones' and Jeffrey's modification of the Zimmermann-Reinhardt method¹¹ as follows:

Place in a 250 c.c. beaker an aliquot of the rock solution, containing not more than 5 c.c. of conc. HCl, boil and reduce with the smallest possible excess of stannous chlorid, added drop by drop while agitating the solution. Wash sides of beaker with distilled water and cool rapidly. Add 10 c.c. of mercuric chlorid solution and stir vigorously for about half a minute.¹² Pour the mixture into a large porcelain casserole or dish containing 20 c.c. of the manganese solution in about 500 c.c. of water which has just been tinted with the permanganate solution.

Titrate with N/40 permanganate solution to original tint and correct result by the volume of KMnO₄ required for a blank containing the same quantity of HCl (diluted), adding 2 or 3 drops of stannous chlorid to the hot solution, cooling, adding 10 c.c. of mercuric chlorid and titrating similarly.

When the rock solution contains carbonaceous mat-

⁶It has been found that when iron oxid is present in considerable excess over aluminum oxid the precipitation of the phosphates is more complete, the combined phosphates are more readily ignited to constant weight, and the precipitate does not become red on ignition.

⁷Ammonium chlorid in large quantity increases the solubility of calcium and magnesium phosphates and decreases the solubility of iron and aluminum phosphates.

⁸This method of adjusting acidity was suggested by F. B. Carpenter and was found to give satisfactory results.

⁹All our work has confirmed Brown's statement (see Wiley, "Principles and Practice of Agricultural Analysis," 2d Edition, 1908, Vol. I, 245) that the separation from calcium under the conditions of the method depends upon sufficient dilution.

¹⁰The contents of the funnel will remain hot if the solution in the beaker is kept hot over a low flame and filtration is fairly rapid.

¹¹Heat over Bunsen to redness before placing over blast in order to prevent loss of precipitate by blowing out of crucible.
¹²Barreby has shown that only a short interval of time is necessary between the addition of mercuric chlorid and manganese sulphate, if the solution is thoroughly agitated. J. A. C. S. XXXVI: 145.

ter it is necessary first to oxidize this with a little potassium chlorate, evaporate to dryness to eliminate chlorine, and redissolve with 5 c.c. conc. HCl and about 10 c.c. of water.

Calculate the Fe_2O_3 found to FePO_4 , using the factor 1.8898, and after deducting from the weight of combined phosphates found, calculate the difference (AlPO_4) to Al_2O_3 .

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PAUL RUDNICK, Chairman.

Committee on Research and Analytical Methods.

MOLYBDIC ACID RECOVERY.*

By C. G. ARMSTRONG.

The large waste of molybdic acid and the difficulty experienced in obtaining the reagent pointed out the great need of a process for its recovery. Numerous methods were tried and cast aside on account of their impracticability or the unnecessary consumption of expensive reagents but finally a method, which is here-with described, was found, which is practical and simple. namely, the precipitation of the acid in HNO_3 by concentration, and its solution in NH_4OH , whereby the molybdic acid is obtained in a condition to be readily used for the preparation of a new stock solution for phosphorus.

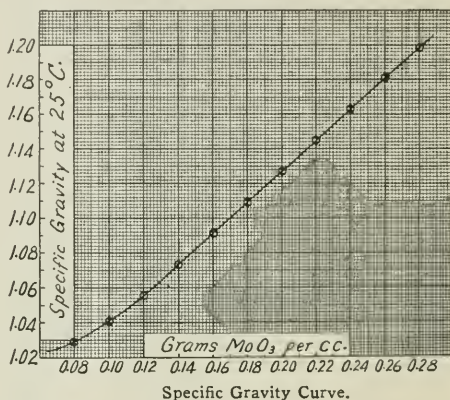
PROCESS.

On account of the fact that phosphomolybdate precipitates are often added to the waste molybdic acid residues in steel analysis, these should be filtered before the recovery process is commenced. This is most conveniently accomplished by means of an asbestos suction filter.

The filtered solution is then placed in a five-liter German flask and supported inverted over a large evaporating dish on a sand bath, allowing but a small amount of the solution in the dish. This method allows a large amount of liquid to be evaporated with little attention. The flask may be refilled until the precipitate of MoO_3 , which forms in the bottom of the evaporating dish, becomes too bulky. Remove the flask and evaporate the solution in the dish until it begins to foam considerably and there is just enough solution left to cover the precipitate and keep the iron in solution. Cool, dilute with one-half volume of cold water, allow to settle and decant. Wash the precipitate thoroughly a couple of times with water by decantation to remove the iron salts and treat with enough 1:1 NH_4OH to fill the dish. A dark brown precipitate will form, due to precipitated iron. The whole is then washed into a large flask, warmed slightly and allowed to stand a couple of hours with an occasional shaking to facilitate solution. When all

is in solution, or after two hours, the liquid may be filtered off by a siphon, sand and asbestos, suction filter into another flask. Arrange the suction tube so that the lower portion of the solution, containing the precipitate, will be the last to come upon the filter, thus preventing troublesome clogging of the filter by the iron precipitate. Add 5 per cent of the original amount of NH_4OH to the solution to make up for that used in precipitating the iron.

This solution contains the MoO_3 as ammonium molybdate and when the specific gravity of it is taken with a hydrometer at 25°C ., by referring to accompanying curve the per cent of MoO_3 present may be



Specific Gravity Curve.

found and then the proper amount of fresh MoO_3 added to bring the concentration up to 0.2825 g. per c.c., which is the concentration of the precipitating solution for phosphorus.

The solution of $(\text{NH}_4)_2\text{MoO}_4$ may be evaporated to dryness and then roasted at 600°C . to MoO_3 , but this is impractical in most cases.

The specific gravity curve was plotted from data obtained by making up solutions of different concentrations and using a pycnometer at 25°C . Various solutions were made up to test the curve and in each case the specific gravity indicated the per cent of MoO_3 to within 0.003 g. per c.c. excepting in concentrations below 0.06 g. per c.c., which concentrations are seldom met with in actual practice.

The solution of $(\text{NH}_4)_2\text{MoO}_4$ in 1:1 NH_4OH when ready to mix with HNO_3 has a concentration of 0.2825 g. per c.c. with a specific gravity of 1.20 (25°C .). This, when mixed with HNO_3 and water, constitutes the regular phosphorus precipitating solution.

The recovery in these tests, which were carried out on large amounts of residues and under actual working conditions, was 93 per cent and the recovered molybdic acid obtained by evaporation and roasting at 600°C . tested chemically pure in all cases (Merck's reagents and their tests).

The cost of recovery is practically nothing except for the gas and time, as no reagents are used which do not go to make up the working solution for phosphorus determinations.

*Analyst, 1909, 31, 306.

*From The Journal of Industrial and Engineering Chemistry.

A STUDY OF SOME RECENT METHODS FOR THE DETERMINATION OF TOTAL SULPHUR IN RUBBER.*

By J. B. TUTTLE and A. ISAACS.

One of the most important problems in the chemical analysis of rubber compounds is the determination of total sulphur. Many investigators have worked on this subject, with the result that different laboratories have their own methods, and comparison of results obtained by these various methods is always difficult, and at times impossible.

This bureau is now using in its routine analysis the method of Waters and Tuttle.¹ In order to learn whether or not the methods for this determination which have been recently published were an improvement, either in accuracy or time required, over the one now in use, and if not, to determine wherein these methods are faulty, this present investigation was undertaken.

GENERAL CONSIDERATION.

The determination of the total sulphur in rubber is far from being a simple problem, involving as it does the simultaneous determination of sulphur in a number of different substances. Sulphur may be found in vulcanized rubber compounds in any of the following forms:

1. Free sulphur.
2. Sulphur combined with rubber *i. e.*, vulcanized rubber.
3. Metallic sulphates, usually lead and barium.
4. Metallic sulphides, usually lead and zinc.
5. Sulphur compounds of fatty acids (from the so-called oil substitutes, or "factis").
6. Sulphur in bituminous substances ("mineral rubbers").

The first and second of these are always present, and the others may or may not be according to the nature of the compound. Any method which has for its purpose the determination of the total sulphur must be adequate to determine any or all of these in widely varying amounts. In our experience in testing material for use in the government departments, the total sulphur has varied from 1.5 to 25 per cent; the free sulphur from practically nothing to 10 per cent; and sulphur in metallic sulphates from nothing up to 6 per cent. The rubber content varied from 20 to 90 per cent, and the quality of the rubber varied from the best to the poorest. We have no quantitative data on the other sulphur-bearing components of rubber goods, but we are certain that they are frequently present and carry appreciable quantities of sulphur.

The almost universal use of litharge (in amounts sometimes 15 and even 20 per cent) in rubber mix-

ings may have considerable bearing on the determination of sulphur by some methods even though the litharge does not in itself contain sulphur. Its effect on the determination of total sulphur will be referred to later in the discussion of the results obtained by the methods investigated.

REVIEW OF RECENT METHODS.

In connection with the previous publication on this subject from this Bureau,² a number of methods in use at that time were investigated and discussed. Since then several new methods have been proposed. Alexander's³ method involving the oxidation of the rubber with sodium peroxide was recommended by Allen⁴ as a "reliable rapid method." Spence and Young⁵ worked on a variation of the electrolytic oxidation first suggested by Gasparini⁶ and afterwards developed by Hinrichsen.⁷ Kaye and Sharp⁸ proposed fusing the rubber directly with a mixture of zinc oxide and potassium nitrate. Ernst Deussen⁹ offered a new idea in an attempt to determine only the free sulphur and the sulphur combined with the rubber. After decomposition with concentrated nitric acid and evaporation, he treated the residue with sodium carbonate and water, and filtered, determining the sulphur in the filtrate colorimetrically. The Joint Rubber Insulation Committee¹⁰ proposed a procedure for the complete analysis of rubber insulation material according to which the total sulphur is determined by fusion with a mixture of sodium peroxide and potassium carbonate. While this method was recommended for 30 per cent Para insulation compounds only, it is desirable to know whether it has a wider application. H. P. Stevens¹¹ suggested a method for correcting for the loss of volatile sulphur in the Henriques method, by absorbing the gases from the determination in alkali and subsequently determining the sulphur thus absorbed. Utz¹² gave a review of the subject in which the method of Kaye and Sharp was compared with that of Frank and Marckwald.¹³ He considered the two methods of equal value.

There are two general methods for determining sulphur in organic compounds which have been used to determine the sulphur in rubber, *viz.*, the Carius and the bomb methods. These are so well known that description at this time is unnecessary. Both of them are considered adequate to determine the total sulphur when modified to suit the conditions peculiar to rubber. Such modifications, however, are time-consuming and render these methods undesirable for the routine analysis of rubber goods. It was therefore

*Waters and Tuttle, *Loc. cit.*

²Gummi Ztg., 18 (1904), 729-730.

³Allen's "Commercial Organic Analysis," 4th Ed., Vol. IV, p. 140, 1911.

⁴Il. Ind. & Eng. Ch., 4 (1912), 413.

⁵Gazz. Chim. Ital. [III], 37 (1907), 426-461.

⁶Chem. Ztg., 23 (1909), 735.

⁷India Rubber Journal, 44 (1913), 1159.

⁸Z. angew. Chem., 24 (1913), 494.

⁹Il. Ind. & Eng. Ch., 5 (1914), 78.

¹⁰Analysis, 39 (1914), 71; India Rubber Journal, 47 (1914), 785.

¹¹Gummi Ztg., 28 (1914), 631-632.

¹²Ibid., 17 (1905), 71.

*From The Journal of Industrial and Engineering Chemistry, in which it is published by permission of the Director of the Bureau of Standards.

¹Bureau of Standards, Reprint 174; Journal of Industrial and Engineering Chemistry, 3 (1911), 734.

not considered necessary to give analytical data in this paper.

SAMPLES.

Even when the assumed total sulphur content is given, this information is not sufficient to enable one to judge the efficiency of the method, since some methods will give low results with materials containing much free sulphur. For the proper interpretation of the results by any method, the entire composition of the samples used, at least as far as the sulphur-bearing constituents are concerned, should be known and reported.

The samples used in this investigation are described in Table I. Sample A was one of the samples used

TABLE I.—COMPOSITION OF SAMPLES.

The figures given are approximate percentages only.

Sample	Description	Rubber content	Sulphur		
			Total	Free	Mineral fillers
A	Insulation	30 Fine Para	5.0	0.5	18 Barytes
B	Suction hose	10 High grade	6.0	0.5	18 Barytes
C	Special	48 Fine Para	4.25 (a)	0.6	16 Barytes 16 Litharge
D	Insulation	28.5 Fine Para	1.75	1.0	4 Litharge
E	Rubber bands	93 High grade	5.0	2.7	2 Litharge
F	Special	12 Coarse Para	8.1 (a)	4	30 Sublimed lead 5 Litharge 2 Barytes 2 Litharge
G	Gasket	55 Poor quality	12.0	8	
H	White tubing	20 Poor quality	21.0	9	36 Barytes

(a) The amount of sulphur added as such in Samples C and F was 2 per cent and 5.1 per cent, respectively.

in the investigations of the Joint Rubber Insulation Committee. Samples B, E, G and H were taken from deliveries on various government contracts.¹⁴ Sample D was prepared especially for the investigations of the Analytical Committee of the Rubber Section of the American Chemical Society. Samples C and F were especially prepared by one of the authors (J. B. Tuttle) at the factory of the Voorhees Rubber Mfg. Co., at Jersey City, N. J., for the purpose of investigating the determination of total sulphur. Great care was taken in the weighing and mixing. The composition was chosen so as to show the effect upon the analysis of the two commonly used sulphates, barytes and sublimed lead, and the vulcanization was controlled so that one of the samples should have a rather large free sulphur content. These two samples have practically the same composition as many that are frequently met with in our routine work and may therefore be considered as representative of such materials.

METHODS COMPARED.

Direct Solution Methods.—1. Spence and Young: conc. HNO_3 , fuming HNO_3 and electrolysis.

2. Deussen: conc. HNO_3 and extraction with Na_2CO_3 .

Direct Fusion Methods.—3. Alexander: Na_2O_2 .

¹⁴In this connection it will be of interest to note that G was taken from a delivery offered on a contract calling for 50 per cent fine Para rubber and not over 3 per cent sulphur other than that present as barytes.

4. Joint Rubber Insulation Committee: Na_2O_2 and K_2CO_3 .

5. Kaye and Sharp: ZnO and KNO_3 .

Solution and Fusion Methods.—6. Frank and Marekwald: fuming HNO_3 , fusion with Na_2CO_3 and KNO_3 .

7. Waters and Tuttle: conc. HNO_3 and Br, fusion with Na_2CO_3 and KNO_3 .

Special Method.—8. Acetone extraction, and separate determination of free and residual sulphur.

The methods as originally described by the various investigators were followed as closely as possible. Whenever it was considered advisable to depart from the original method, the reasons therefor are given. Unless otherwise stated, 0.500 gram was taken for each determination. The "fusion mixture" used was composed of equal parts of sodium carbonate and potassium nitrate. Fusions were made with the gasoline gas generator described by Waters.¹⁵ The barium sulphate precipitates were allowed to stand over night before filtering, and were ignited and weighed in porcelain crucibles. In soluble residues were examined for sulphur, the amounts of which, if present in appreciable quantities, are given. The reagents used were tested and found to be practically free from sulphur, so that no corrections are necessary on their account. Methods 4, 6, 7 and 8 are intended to determine the total sulphur, while 1, 2, 3, and 5 are intended for the determination of sulphur other than that present as insoluble sulphates.

1. *Spence and Young.*—The rubber was treated with 5 cc. of concentrated nitric acid, and heated gently. When the first reaction was over, about 50 cc. (exact amount was not specified by the authors) of fuming nitric acid were added and the solution electrolyzed. As a source of current, an 8-volt storage battery was used. This was connected directly to the platinum electrodes. The resistance of the electrolytic cell was such that the current was usually between 2 and 3 amperes, though at times it was low as 1 ampere. After two or three hours, the current was discontinued, the electrodes removed, 1 gram of potassium nitrate¹⁶ was added and the solution evaporated to dryness. The nitric acid was completely removed with hydrochloric acid by several evaporations. A few drops of hydrochloric acid were added, the residue was treated with hot water and filtered. The sulphur in the filtrate was precipitated as usual. The insoluble matter filtered off above was fused with 5 gms. of fusion mixture, extracted with hot water, filtered, and after acidification the sulphur in the filtrate was precipitated as usual.

2. *Deussen.*—The Deussen method was not followed exactly as given by the author. The rubber was treated in a porcelain crucible with concentrated

¹⁵Ill. Ind. & Eng. Ch., 5 (1913), 853.

¹⁶Spence and Young add 1 gm. of sodium carbonate, but, inasmuch as this in solution is changed to sodium nitrate, we used potassium nitrate, which serves the same purpose and obviates the spattering caused by the addition of a carbonate to the hot concentrated acid.

nitric acid and covered. After heating for a short time, the cover was removed and the solution evaporated to dryness. The residue was treated with sodium carbonate and water, and after heating, the solution was filtered. Up to this point the original method was followed exactly. Deussen reduces the sodium sulphate to sulphide and determines the latter colorimetrically. In order to avoid any error introduced by this procedure and to obtain a better comparison with the other methods, we added potassium nitrate to the filtrate, evaporated to dryness and fused. The sulphur in the cooled melt was determined as under the Waters and Tuttle method. The insoluble residue from the sodium carbonate filtration was fused with 5 grams of fusion mixture and the sulphur determined as usual.

3. *Alexander*.—The Alexander method, as given in Allen's "Commercial Organic Analysis," is said to be rapid and reliable. The rubber is intimately mixed with 16 grams of sodium peroxide in an iron crucible provided with a lid through which a small hole has been bored. The combustion is started by introducing through this hole a red hot iron wire. No further heating is required. When the mass is cool it is dissolved in water, the crucible, lid and wire are removed, the solution is acidified with hydrochloric acid and boiled, then filtered if necessary and the sulphate precipitated by means of barium chloride.

4. *Joint Rubber Insulation Committee*.—The rubber was fused with 4 grams of sodium peroxide and 6 grams of potassium carbonate. The cooled melt was extracted with hot water to which some bromine water had been added. The solution was filtered, acidified with hydrochloric acid and evaporated to dryness to dehydrate silica. About 400 cc. of water were added, the solution made slightly acid with hydrochloric acid, filtered, and the sulphur in the filtrate determined as usual.

5. *Kaye and Sharp*.—The rubber was mixed with 4 grams of zinc oxide and 2 grams of potassium nitrate, placed in a crucible (both iron and porcelain were used), and covered with a layer of zinc oxide about 1 cm. deep. This was carefully heated, at first with a low, and afterwards with a full Bunsen flame. The crucible and contents were placed in a beaker, covered with water and heated; the solution was acidified with hydrochloric acid and filtered. The sulphur in the filtrate was determined as usual.

The insoluble residue filtered off from the hydrochloric solution was fused with 5 grams of fusion mixture and the sulphur determined as under the insoluble matter in the Spence and Young method.

6. *Frank and Marckwald*.—The rubber was treated with about 20 to 25 cc. of fuming nitric acid in a porcelain crucible, the vessel covered with a watch glass and allowed to stand over night. The solution was evaporated to dryness, the residue fused with 5 grams of fusion mixture, extracted with hot water

and filtered. The filtrate was acidified with hydrochloric acid and the sulphur precipitated as usual.

7. *Waters and Tuttle*.—The rubber was treated in a porcelain crucible with 25 cc. of concentrated nitric acid saturated with bromine, the vessel covered with a watch glass and allowed to stand one hour. It was heated on a steam bath for one hour and then the cover was removed and the solution evaporated to dryness. The residue was fused with 5 grams of fusion mixture, extracted with hot water, filtered, the filtrate acidified with hydrochloric acid and the sulphur precipitated as usual.

8. *Extraction With Acetone*.—Some determinations were made by extracting 2 grams of rubber with freshly distilled acetone for eight hours. The acetone solution was evaporated to dryness, distilled water and bromine added, the solution heated until colorless, filtered, and the sulphur in the filtrate determined as usual. The insoluble residue was examined for sulphur by fusing with 5 grams of fusion mixture. The amount of sulphur thus found was scarcely ever more than a few tenths of a milligram.

The extracted rubber was dried at about 60° C. and the sulphur determined according to the method of Waters and Tuttle. The sum of these various determinations should be the total sulphur.

DISCUSSION OF RESULTS.

Although the method of Waters and Tuttle is No. 7, it has been considered advisable to discuss it first since it is the most reliable and accurate method we have found for the determination of total sulphur. The reaction proceeds slowly without any very great evolution of heat so that there is little or no chance of losing free sulphur. Even when the free sulphur is very high the method is adequate to determine it with accuracy. A large number of determinations were made, and the results are concordant and agree with the calculated results in samples of known composition.

The Waters and Tuttle method has been in use at the Bureau of Standards for a number of years, and during that time has frequently been used in determining the total sulphur in samples of known composition. The results have invariably been satisfactory even when obtained by comparatively inexperienced analysts.

The methods which have been compared in the course of this investigation may be divided into two classes, viz., those for the determination of the total sulphur, and those for the determination of sulphur other than that present in the insoluble sulphates. They may be further classified, according to the method of attack employed, as follows: direct solution, direct fusion, and solution and fusion methods.

The methods which have for their object the determination of sulphur other than that present in the insoluble sulphates (Nos. 1, 2, 3, and 5), attempt to separate the insoluble sulphates by filtration. Spence and Young, Alexander, and Kaye and Sharp filter

from an acid solution. The securing of correct results by this method is based upon the obviously incorrect assumption that the lead sulphate originally present would remain insoluble while that formed from the litharge would be completely dissolved. Deussen filters from an alkaline carbonate solution, but this procedure is open to the objection that lead sulphate will react with sodium carbonate solution with the formation of soluble sodium sulphate. It is apparent, therefore, that such methods cannot give reliable results since their basic principles are faulty.

Considering the methods as classified according to the mode of attack, we find that the direct solution methods (Nos. 1 and 2) employ concentrated nitric acid. The use of this reagent in the determination of the total sulphur in rubber was first suggested by Henriques, and many investigators have shown that

its use gives low results, probably on account of the loss of free sulphur. Even when the sulphur which is remaining in the insoluble residue is included with that in the filtrate, the sum does not equal the calculated value.

The direct fusion methods (Nos. 3, 4 and 5) give results which are satisfactory only when the free sulphur content is relatively low. In view of the results obtained by the other fusion methods, it was not considered necessary to make any determinations by the Alexander method. The reaction between rubber and sodium peroxide often proceeds with explosive violence, particularly so when, as in this method, the sodium peroxide is not diluted with some less active flux. The more important points have been demonstrated by the results on the other methods, namely, (1) that the direct fusion may give low results, and

RESULTS OF TESTS FOR SULPHUR.

Method.	1—Spence and Young.			2—Deussen.			4—Joint Rubber Insulation Committee		5—Kaye and Sharp.			6—Frank and Marcwald		7—Waters		8—Extraction with acetone.		
	Fil-trate.	Resi-due.	Total.	Fil-trate.	Resi-due.	Total.	Fil-trate.	Resi-due.	Fil-trate.	Resi-due.	Total.	Total.	Total.	Total.	Total.	Ex-tracted.	Resi-due.	Total.
A							4.90						4.87					
B				4.53	1.66	6.19	6.26	3.63	2.43	6.06	6.00	6.29	0.51	5.74	6.25			
				4.84	1.41	6.25	6.31				6.18	6.30	0.40	5.90	6.30			
				3.84	2.74	6.58					6.26	6.33	0.44	5.85	6.29			
				3.89	2.65	6.54					6.28	6.35						
												6.42						
												6.42						
												6.43						
												6.44						
C				3.19	0.88	4.07	4.09	3.38	0.66	4.04	4.19	4.17	0.61	3.59	4.20			
				2.55	1.52	4.07	4.13	2.45	1.68	4.13	4.20	4.18	0.63	3.60	4.23			
							4.19	3.32	0.86	4.18	4.28	4.20	0.60	3.64	4.24			
							4.31					4.22						
												4.23						
												4.25						
D							1.73					1.65						
							1.76					1.67						
							1.78					1.70						
							1.80					1.73						
							1.81					1.75						
							1.83					1.78						
E	4.91											4.95						
												5.15						
												5.22						
F	5.39	2.33	7.71	7.47	0.47	7.94	7.78	6.89	0.21	7.10	7.72	7.90	3.59 ^(a)	4.22	7.81			
	6.90	0.88	7.78	7.74	0.22	7.96	7.80	6.81	0.38	7.19	7.78	7.96	3.26 ^(a)	4.81	8.07			
	6.42	1.36	7.78				7.83				7.80	7.96	4.02	4.06	8.08			
	5.04	2.75	7.79				8.01				7.86	7.96	4.04	4.04	8.08			
	4.67	3.17	7.84				8.02				7.88	8.00						
	5.05	2.81	7.86									8.01						
	4.52	3.38	7.90									8.02						
	4.71	3.26	7.97									8.09						
												8.11						
												8.12						
												8.12						
												8.13						
G	11.49	0.35	11.84	5.52	4.04	9.56	10.98	9.89	0.04	9.93	11.56	11.96	8.31	3.69	12.00			
	11.45	0.40	11.85	5.51	4.71	10.22	11.34	9.77	0.57	10.34	11.64	12.00	8.14	3.88	12.02			
	11.46	0.39	11.85	8.33	2.81	11.14	12.04	9.80	0.55	10.35		12.04	8.06	3.97	12.03			
	11.52	0.34	11.86	7.96	3.43	11.39	12.10	10.74	0.03	10.77		12.08						
	11.36	0.53	11.89					10.42	0.41	10.83		12.16						
	11.57	0.32	11.89									12.18						
	11.43	0.47	11.90									12.19						
	11.56	0.34	11.90									12.20						
	11.47	0.45	11.92									12.23						
	11.44	0.48	11.92									12.29						
H				15.77	4.94	20.71	20.52	15.68	5.20	20.88	20.71	21.09	9.60	11.52	21.12			
				15.69	5.16	20.85	20.68					21.16						
							20.74					21.20						
							20.83					21.30						
												21.32						
												21.36						
												21.40						

^(a) These samples were not completely extracted.

(2) that the filtering of the solution of the melt after the addition of acid gives results which have no relation to sulphur it is desired to determine.

Although the reaction during the fusion in the Kaye and Sharp method is not attended by an explosion, the results show that it is open to all the other objections which have been made above; hence it cannot be relied upon to give results which have any significance.

The results obtained by the method of the Joint Rubber Insulation Committee (No. 4) are accurate when the free sulphur is low, as it is in insulation compounds, so that it may be relied upon to do all that this committee has claimed for it. This has been also substantiated by the work of the Analytical Committee of the Rubber Section of the American Chemical Society.¹⁷ Whenever the free sulphur content is high, our results indicate that this method has the same serious defect as the other direct fusion methods.

The methods which require both solution and fusion yield the most satisfactory results. One of these (the Waters and Tuttle method) has already been referred to. The Frank and Marckwald method is at times very satisfactory, but unfortunately it does not seem reliable with large amounts of free sulphur. The reaction between the rubber and the fuming nitric acid is at times very violent and considerable heat is evolved. In fact in several cases, by adding only 1 or 2 cc. of the acid, the heat was so great as to cause the rubber to take fire. It seems probable that this heating is responsible for the loss of sulphur and the consequent low results.

In view of the fact that the free sulphur can be determined by several methods (one of which has already been described) with considerable accuracy in the acetone extract, and since this determination is usually made in analyses of vulcanized rubber goods, it is possible, and in some cases may be convenient, to determine the total sulphur by adding to the result for free sulphur, the amount found in the residue after acetone extraction. Such a method would have the advantage of first removing the free sulphur, which has been found to be one of the most disturbing factors in many of the methods for the determination of total sulphur. Our experience indicates that accurate results can be obtained by this method.

We have determined the sulphur remaining in the rubber after the acetone extraction, by the Waters and Tuttle method. It is more than possible that other methods will be equally efficient.

OUTLINE OF THE METHOD ADOPTED BY THE BUREAU OF STANDARDS.

As the result of this and other investigations and the experience of the Bureau of Standards, extending over some years, we believe that the Waters and Tuttle method is the most reliable and it has been adopted for use in the routine work there. The determination is made as follows:

Half a gram of rubber is placed in a porcelain crucible of about 100 cc. capacity, 20 to 25 cc. of concentrated nitric acid which has been saturated with bromine, are added, the crucible covered and allowed to stand for 1 hour. It is then heated gently for 1 hour, after which the cover is removed, rinsing it with a little distilled water, and the solution is evaporated to dryness.

Five grams of fusion mixture (1 potassium nitrate; 1 sodium carbonate) and 3 or 4 cc. of distilled water are added, the mixture is digested for a few moments on the steam bath and then spread halfway up the side of the crucible to facilitate drying. The drying is done on a steam bath or electric hot plate; in the latter case care is taken to avoid spattering caused by possible overheating. When dry, the mixture is fused over a sulphur-free flame until all the organic matter has been destroyed and the melt is quite soft. The crucible and contents are cooled, placed in a 600 cc. beaker, covered with distilled water and heated on the steam bath for 3 or 4 hours. The solution is then filtered and the insoluble matter washed thoroughly. The combined filtrate and washings should amount to about 500 c.c. About 7 or 8 cc. of concentrated hydrochloric acid are added, the beaker covered, and the solution heated almost to boiling. The solution is now tested and if necessary made slightly acid toward Congo paper; if the directions have been followed exactly, there should be a slight excess of acid present. Ten cc. of 10 per cent barium chloride solution are added, and the solution is allowed to stand over night. The precipitated barium sulphate is filtered off and ignited over a small Bunsen flame, care being taken to see that the filter paper does not inflame. The barium sulphate is calculated to sulphur by means of the factor 0.1374.

SUMMARY.

It is shown that the methods which have been proposed for the determination of the total sulphur other than that present as insoluble metallic sulphates, are not satisfactory.

It is shown that loss of sulphur is likely to occur in the direct fusion methods, and this loss is apt to increase with increasing free-sulphur content.

The method of Waters and Tuttle is recommended for the determination of total sulphur. This method is accurate and comparatively rapid, and has given satisfactory results in the hands of a number of analysts over a rather extended period of time. A new suggestion is offered, namely, to determine separately the free sulphur and the sulphur remaining after the acetone extraction, reporting the sums of the two quantities of total sulphur. This procedure eliminates the troublesome effect of the free sulphur upon the determination of the total sulphur.

¹⁷J. Ind. & Eng. Ch., 6 (1914), 514-518.

THE DETERMINATION OF FAT IN ICE CREAM BY THE BABCOCK METHOD.*

By C. A. A. UTT.

The determination of fat in ice cream by the Babcock method is simple, desirable, and accurate, if properly conducted. In this laboratory the hydrochloric-acetic acid method has not been found satisfactory in most cases. If much gum thickener, gelatine, or condensed milk, has been added, a white precipitate comes up in the neck of the bottle on the last addition of water, obscuring the fat column, thus preventing an accurate reading.

The following method, making use of a mixture of sulphuric and acetic acids, was developed in this laboratory. It has been in use over a year and has given excellent results on commercial ice cream. It has also been checked against ice cream mixtures of known fat content. Since developing the method the author has been told that there is such a method in existence but he has been unable to locate it. The details are offered for what they may be worth.

PROCEDURE.

A—Mixing the Sample.—Warm the sample to 40° C. and mix by pouring and stirring. If the fat has separated, a few granules of powdered sodium hydroxide may be necessary to aid in the emulsification.

B—Weighing.—Weigh 9 grams of the well-mixed sample into a 10 per cent Babcock milk bottle. A pipette, with a large outlet, but sufficiently small to fit in the neck of the bottle, is desirable. Nearly the required amount can be added to the bottle by blowing and the remainder dropping.

C—The Babcock Process.—Make up a mixture of equal parts by volume of commercial sulphuric acid (sp. gr. 1.83) and glacial acetic acid.¹ Allow this mixture to cool before using. Add 12 to 15 cc. of this mixture to the ice cream in the Babcock bottle at about the same temperature. Shake the mixture, using a rotary motion. Place the bottle in a steam bath or hot water, and heat with occasional shaking until it turns a dark chocolate color. Remove the bottle from the steam bath and allow it to stand 10 minutes. Place in a centrifuge (preferably a steam centrifuge) and whirl 10 minutes. Shake the bottle again, using a whirling motion. Fill to the neck with hot water and mix. A precipitate sometimes forms on the addition of hot water. This can usually be destroyed by adding a few cc. of the acid mixture. Whirl 3 minutes and add boiling water to bring the fat column in the neck of the bottle. Whirl 2 minutes. Read from the bottom of the fat column to the extreme top of the meniscus and multiply the reading by 2. If a centrifuge without a heating device has been used, the bottle should be held in water at 55°

C. for 10 minutes before reading. Chalk, powdered calcium carbonate or talc rubbed on the graduated neck of the bottle facilitates reading the fat column.

A few examples will illustrate the value of the method:

No.	Ice cream mixture containing Thickener.	Butter fat (%)	Per cent butter fat found.				Av. Diff. Per cent.
			A	B	C	D	
1	None	13.60	13.40	13.50	13.70		13.53 0.07
2	None	15.67	15.60	15.60	15.60	15.60	15.60 0.09
3	Gum tragacanth	13.54	13.50	13.40	13.60	13.60	13.50 0.04
4	1 Rennin tablet	12.22	12.20	12.00	12.30		12.15 0.07
5	Condensed milk	16.20	16.00	16.00	16.20		16.07 0.13
6	Condensed milk and gelatin....	16.60	16.40	16.10	16.60	16.40	16.45 0.15

SUMMARY.

The method as outlined, using a mixture of sulphuric and acetic acids, gives good results in the determination of fat in ice cream. Checks were obtained in ice cream mixtures made up according to various formulas within from 0.04 to 0.15 per cent of the amount occurring in the mixtures.

The above method has been in constant use for over a year in this laboratory and uniformly good results have been obtained on commercial samples of ice cream.

ROCK ASPHALT IN PHILIPPINES.*

The chemical analyses have been completed upon representative samples of the deposit of rock asphalt discovered by the division of mines, Bureau of Science, in Leyte, and the results justify the hopes already expressed [see Commerce Reports for July 22, 1915] that this material would prove suitable for paving.

Samples of the poorer rock, according to analyses just completed, contain 6 per cent of bitumen. The average rock contains from 7 to 9 per cent bitumen, and rich portions near the base of the deposit contain as much as 62 per cent bitumen. The analyses show, further, that the bitumen consists largely of asphaltene, and that the proportion of paraffin, a constituent which is undesirable in asphalt for paving, amounts to less than one-half of 1 per cent of the total bitumen. The results of the analyses tend to remove the doubt which has been felt as to the possibility of using the Leyte rock asphalt for paving. The purer bitumens in Leyte, associated with the rock asphalt, are known to be high in paraffin and to form brittle solids unsuitable for pavement, but the rock asphalt itself appears to be free from these objections and to be very similar, so far as analyses reveal its character, to rock asphalts which are successfully used for paving in the United States and Europe.

It is probable that a trial pavement will be constructed from the Leyte rock asphalt, upon which observations can be made to determine absolutely the suitability of this material for paving.

*From The Journal of Industrial and Engineering Chemistry. We use Grasse's Chemical Co. glacial acetic acid, 99.5 per cent, strictly C. P.

*From Daily Commerce Reports.

METALLURGY.

THE HEAT TREATMENT OF IRON AND STEEL IN A NEUTRAL ATMOSPHERE.*

By ALFRED H. WHITE AND HOMER T. HOOD.

When iron or steel is heated to a high temperature, for forging or heat treatment, in a furnace where it comes into direct contact with flames, smoke, gases or other oxidizing atmosphere, its surface becomes first decarburized and then oxidized and covered with scale. Not only is the actual loss of metal in heating for the forge of considerable importance, but the surface decarburization is becoming of greater importance in view of the high standards demanded by the tool manufacturers and the automobile industry. It has shown that metal received from the rolling mill may show decarburization to a depth of 0.015 inch, and that the metal to that depth must be removed from the surface to eliminate all trace of decarburization. Decarburization due to heat treatment at lower temperatures is also evident, though not so serious. It is possible to avoid these undesirable changes by heating the metal in an externally fired muffle filled with an inert gas, such as nitrogen. Externally fired muffles, however, always show a low thermal efficiency, and there are difficulties in the production and utilization of nitrogen. Since heating in illuminating gas alone has been found to cause carburization of steel, while heating in the ordinary products of complete combustion causes oxidation, it seemed that somewhere between these two extremes there should be a composition practically neutral in its effect on steel. It seemed feasible to construct a muffle furnace with semi-direct firing, in which a mixture of gas with a small amount of air should burn within the muffle to form a neutral atmosphere, and subsequently burn with more air around the muffle and thus utilize the full thermal energy of the gas.

Whenever a number of substances are allowed to react with each other for a sufficiently long time they finally come to a definite stable condition called equilibrium. This equilibrium will vary with the temperature, pressure and concentration of the substances. A full solution of the problem here presented would call for a study of the equilibrium between the various possible compounds formed by the interaction of iron, carbon, hydrogen and oxygen. Such a complete solution, however, would demand a prohibitive amount of experimental work. For practical purposes it is not absolutely necessary that the atmosphere be strictly neutral, for the rate of reaction decreases as equilibrium is approached, so that there will

not be serious change in the surface of the metal if the time of heating be short, even though there is a tendency towards a reaction in one direction or the other.

Although the equilibrium in the complicated system—iron, carbon, hydrogen, oxygen—has not been worked out, the simpler system—iron, carbon, oxygen—has been studied by several authors and is summarized by Arndt. From his figures it may be seen how great an influence is exerted by temperature. At 1100° F. iron will not be oxidized by a gas that carries 75 parts of CO₂ to 25 parts of CO, while at 1400° F. not more than 15 parts of CO₂ can be allowed to 85 of CO, if oxidation is to be avoided. The figures have not been worked out for higher temperatures, but it is evident that still smaller proportions of carbon dioxide, the oxidizing gas, must be maintained if oxidation is to be avoided at high temperatures. These considerations make it evident that it will be difficult to use producer gas for the production of a neutral atmosphere at high temperatures since its active constituent, CO, is almost necessarily associated with several per cent of CO₂ as it leaves the producer, and any attempt to produce a partial combustion in the presence of the steel would necessarily produce an oxidizing atmosphere.

Illuminating gas presents better possibilities than producer gas on account of the high percentage of hydrogen and hydrocarbons, which act as reducing agents. But in the flame from illuminating gas there will be present not only carbon dioxide as an oxidizing agent but also steam; and if oxidation of the metal is to be avoided the sum of these oxidizing gases must be kept low. A mixture of illuminating gas and air containing less than 80% of air, is no longer explosive and will not support combustion unless it receives heat from some external source. This condition is approximately realized in the ordinary Bunsen flame. Arndt in his summary of the work of various authors gives the average composition of the inner Bunsen flame to be:

Reducing Gases.	Oxidizing Gases.	Inert Gases.
CO 2.2%	CO ₂ 7.2%	N 66.6%
H ₂ 2.8%	H ₂ O 20.2%	
CH ₄ 1.0%		
6.0%	27.4%	66.6%

The oxidizing gases in the inner cone are therefore four and a half times as great as the reducing gases, and the mixture must exert a strongly oxidizing action on steels at high temperatures. If the amount of carbon dioxide and water vapor is to be kept low enough not to give an oxidizing flame, there will not be enough air in the mixture to support com-

*From The American Gas Light Journal.

bustion under ordinary conditions. A part of the problem is therefore to design a furnace that will give high temperatures, and yet burn a very rich mixture of gas and air.

The Attainment of High Temperatures in a Neutral Atmosphere.—In ordinary complete combustion of gases the final products of combustion are CO_2 and H_2O . In the method here proposed the combustion within the muffle will be incomplete, and it is desirable to know what temperature it is possible to attain under such circumstances. To calculate the theoretical combustion temperature, it is necessary to calculate the volume of the several products of combustion and the amount of heat evolved in the combustion. The gas available was an unenriched coal gas with an average heating value of somewhat over 600 B. T. U., and it was found possible to burn this in the furnace described with two volumes of air. The calculations for volume of products of combustion and theoretical flame temperature are shown in Tables I. and II. The volume of the products of combustion is calculated in two ways, and check closely. The simplest method is to work from the percentages of nitrogen, and by this method the volume of combustion gases from one cubic foot of gas and two of air is calculated from Table I. as,

$$\frac{12.5 + 153.4}{52.6} = 3.16 \text{ cubic feet.}$$

The calculation based on the hydrogen contained in the incoming and outgoing gases is,

$$\frac{120.2 + 6.0}{39.7} = 3.18 \text{ cubic feet.}$$

The average of these, 3.17 cubic feet, is taken as the volume of the products of combustion of one cubic foot of gas with two of air. Applying this figure to the values for carbon in the gas as given in Table III. and multiplying the 18.7 volumes of carbon in the combustion gas by 3.17, 59.2 is obtained as corresponding to the carbon (calculated as gas) in 100 volumes of the inflowing gas. The actual figure for the inflowing gas is 60.6, which is 1.4 volumes greater than the amount found in the combustion gases. This corresponds to the free carbon which produced a slightly luminous flame within the retort.

The net heating value of the gas is used in these calculations for temperature, since the water formed will escape from the furnace in the form of steam. The specific heats used are the mean specific heats per cubic foot for the range up to 2,200° F. The theoretical combustion temperature that can be attained when one cubic foot of cold gas is burned with two cubic feet of cold air is 2,250° F., as is shown in Table II. Still higher temperatures would be theoretically possible if the gases of incomplete combustion could be completely burned in a secondary operation and made to give up their heat to the incoming air.

TABLE I.—VOLUME OF PRODUCTS OF COMBUSTION.

Obtained from 1 cubic foot gas and 2 cubic feet air.

Constituent.	Percentage composition of—					
	Gas.		Air.		Products of combustion	
H_2O vapor	3.0		3.0		15.6	
CO_2	1.8				2.5	
Illum. (C_2H_4)	4.7				0.9	
O_2	1.1		20.3		0.0	
CO	6.9				9.8	
CH_4	33.1				2.8	
H_2	36.9				15.8	
N_2	12.5		76.7		52.6	
Total	100.0		100.0		100.0	
Total Vol. H_2 Total Vol. N_2 Total Vol. C						
Entering into Entering into Entering into						
100 200 vols. 100 200 vols. 100 vols.						
vols. vols. comb. vols. vols. comb. vols. comb.						
Constituent.	gas.	air.	gas.	gas.	air.	gas.
H_2O	3.0	6.0	15.6			
CO_2					1.8	2.5
Illum. (C_2H_4) ..	4.1		2.7		16.8	3.6
CO					6.9	9.8
CH_4	66.2		5.6		33.1	2.8
H_2	36.9		15.8			
N_2			12.5	153.4	52.6	
Total	120.2	6.0	39.7	12.5	153.4	52.6

TABLE II.—THEORETICAL FLAME TEMPERATURE OBTAINED FROM 1 VOL. GAS AND 2 VOLS. AIR.

Net Heating Value of 1 Cubic Foot Illuminating Gas Burned Completely.

Constituents. of Gas.	Net Heating Value		Net Heating Value	
	B.T.U.	per cu. ft. in Gas.	B.T.U.	per cu. ft. in Gas.
Illuminants	2600.	4.7	122.0	
CO	326.	6.9	22.5	
H_2	275.	36.9	103.0	
CH_4	900.	33.1	300.0	

Net heating value per cubic foot (B. T. U.) 547.5

Net Heating Value of 3.17 Cubic Feet of Gases Produced by Burning 1 Vol. Gas and 2 Vols. Air.

Illuminants	2600.	0.9	23.4
CO	326.	9.8	32.0
H_2	275.	15.8	43.1
CH_4	900.	2.8	25.2

Net heating value per cubic foot (B. T. U.) 121.0

Net heating value from 3.17 cu. ft. (B. T. U.) 393.

Solid carbon in 3.17 cu. ft. = 0.0005 lb. (B. T. U.) 400.

Net heating value of gas on complete combustion... 547.

Net heating value of products of incomplete combustion 400.

Heat liberated during incomplete combustion..... 147.

MAXIMUM THEORETICAL TEMPERATURE OF PRODUCTS OF COMBUSTION.

Constituents.	Vol. in cubic foot.	Mean Sp. Ht. Heat Absorbed	
		B. T. U. per cu. ft. for 1° F.	Interval Rise in Temperature.
H_2O	0.156	0.0245	0.0038
CO	0.025	0.0302	0.0007
$\text{CO}-\text{H}_2-\text{N}_2$	0.782	0.0189	0.0148
CH_4 -Illum.	0.037	0.0540	0.0020

(B. T. U.) 0.0213

Heat absorbed by 3.17 cubic feet for rise in temperature of 1° F. = $3.17 \times 0.0213 = 0.0675$ B. T. U.

Heat available 147.0 B. T. U.

Theoretical consumption temperature, above room temperature 147

$\frac{147}{0.0676} = 2,180^\circ \text{ F.}$

Assume room temperature to be 70° F. 70°

Theoretical combustion temperature 2,250° F.

Experimental Work.—The laboratory furnace finally developed is shown in Fig. 1. The heating chamber is a quartz tube, into whose lower end is luted a Meker burner with connections by which air and gas supply can be metered. The rich gas mixture is heated as it rises through the hot quartz tube and is ignited near the walls soon after reaching the hot zone. The heat of this initial combustion ignites the remainder of the gas so that by the time the mixture had risen half way in the tube, combustion is complete, and the upper half of the tube is entirely free from flame. The pieces of metal were heated in these hot gases of controlled composition. As the gases passed out

Heat liberated during incomplete combustion, 147 B. T. U.

Thus 147 out of the possible 547 heat units, or 27%, were liberated in the primary combustion around the metal, and the remaining 73% liberated in the secondary combustion around the muffle. No attempt was made to utilize the heat of the stack gases to preheat the primary air, but this might well be done in a large furnace. It would be possible in this way to burn richer mixtures of gas and air than was possible with the small furnace.

In order to sample the gas within the muffle, it was necessary to cool them very rapidly, so as to avoid change in composition. A capillary quartz sampling tube with its upper part water-jacketed was inserted through the hole in the cover, and in this way there was a temperature drop of about 1,830° F. in one inch. From the capillary tube the gas was passed through a weighted calcium chloride drying tube to absorb the water vapor, and then into a two-litre gasometer from which samples were taken for analysis.

Since rapidity of oxidation is a function of the extent of surface of the metal, and it was desired to get as positive results as possible, the metal tested was in the form of very fine wire. A piece of No. 34 soft iron wire (0.005" diameter) about 10 feet long, was wound into a small spiral and weighed. It was then hung on a hook of heavy wire and suspended in the upper part of the central tube of the furnace, in the gases that had come to equilibrium in the lower part of the tube. The coil of wire was usually left in the furnace for an hour—an excessively severe test. Special precautions had to be taken in removing the hot wire from the furnace, as, if removed while hot, it would be badly oxidized in the few seconds' exposure to the air. In order to cool it before taking out, a small piece of gas pipe with one end closed was lowered into the furnace and the sample placed inside. Here it was cooled by radiation to the cold walls of the pipe, and the pipe was removed before it had time to get hot. It is probable that even this method allowed slight oxidation, as a little air would be left in the pipe. After removing, the sample was weighed and a colorimetric determination for carbon made. The increase in weight represented the amount of oxygen absorbed to form magnetic oxide (Fe_3O_4). This oxide contains 2.61 parts of iron for each part of oxygen, so that an increase in weight of 1% means that 2.6% of iron oxidized. This wire was very nearly 0.005" in diameter and a pound of it had a surface of about 20 square feet. If 25% of it was oxidized the depth of penetration of the oxidation would be only 0.00035" and a 2% increase in weight, equivalent to 5.22% oxidation would mean a depth of oxidation of only 0.00005". So it is seen that a very slight thickness of oxide is easily measured. Since this wire contained initially only 0.04% of carbon, an analysis of the treated wire did not show the decar-

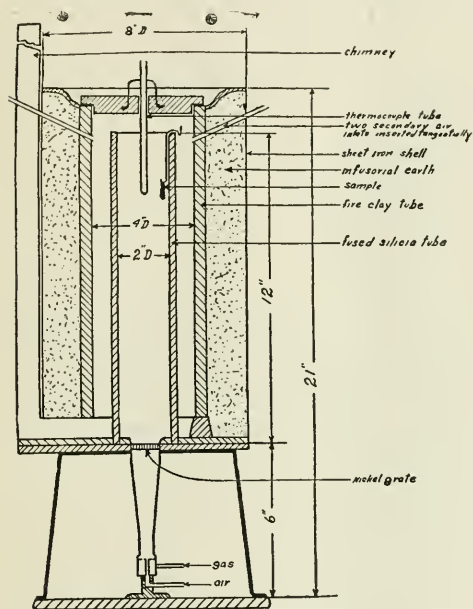


Fig. 1.—Laboratory Furnace for Heating Metals in Neutral Atmosphere.

of the quartz tube and turned to descend the annular space, more air was mixed with them, and the combustion completed as they passed down around the outside of the muffle. By this method the muffle was kept hot, and loss by radiation prevented, and the rich gas mixture brought up to kindling temperature by the radiant heat from the muffle; so that a mixture that would not burn in an open flame could be burned easily. Burning a mixture of two parts of air with one of gas, a temperature of 2,200° F. was easily maintained within the muffle.

The thermal efficiency of the furnace thus operated is indicated in Table IV, from which the following figures are taken:

Net heating value of gas on complete combustion, 547 B. T. U.

Net heating value of products of incomplete combustion, 400 B. T. U.

burization very accurately, so further tests were made on steel piano wire. The smallest size of this wire at hand was No. 28, 0.014" in diameter; and the calorimetric test showed about 1.25% of carbon before heating, but practically no carbon after heating for an hour at temperature of 2100-2200° F. Under these circumstances a 1% gain in weight meant a 2% gain in oxygen since the wire lost about 1% of carbon during the heating process. This 2% increase in oxygen meant 5.2% oxidation, and corresponded to a depth of oxidation of 0.00175". If the piece did not change in weight, but 1% of the carbon was lost and replaced by 1% of oxygen, then the depth oxidation would be 0.0008".

Affect of Heating Mild Steel in a Neutral Atmosphere.—Data of tests on the iron wire with 0.04% carbon given in Tables III. and IV. It will be noted that the tests are excessively severe, the fine wire being directly exposed to the gases at 2100-2200° F. for from 35 minutes to 2 hours. The figures in Table III. are arranged according to the volumes of air used. With 2.5 volumes of air to one of gas the fine wire is, after an hour's heating, converted almost completely into oxide, and with 2.4 volumes of air the oxidation shown by the increases in weight amounts to 56%. (Exp. 10.) However, with this fine wire, even this high oxidation gives a film of oxide only 0.0008" in thickness, a thickness negligible in ordinary work. The composition of the gases surrounding the wire while being heated is shown in Table IV. The oxidizing agents (carbon dioxide, steam and a trace of oxygen) amount in Test 10 to 18.3%, and the reducing agents, consisting of (carbon monoxide and hydrogen with a small percentage of methane), amount to 27.8%. The ratio of the reducing gases to the oxidizing gases is 1.52.

With slightly richer gas mixtures the oxidation, even as shown by the sensitive test of increase in weight, becomes very small. With less than two volumes of air the flame in the inner muffle became distinctly yellow, seemingly a good indication that oxidizing conditions had disappeared, for the samples (Nos. 6, 9 and 12), heated under these conditions,

showed almost no increase in weight and no brittleness on bending, and retained their silvery metallic lustre. Analysis of the gases from the muffle showed the ratio of reducing to oxidizing gases to be from 1.76 to 1.98. It was stated in the earlier part of this paper that the work on carbon monoxide had shown that in order to prevent oxidation of iron it was necessary to have more than five times as much CO as

Test No.	Average for illuminating gas used.		Composition of gases after partial combustion.				
	3.	6.	7.	10.	12.		
H ₂ O (vapor) . . .	3.1	14.6	15.6	14.7	15.6	13.9	
CO ₂ . . .	1.8	3.2	2.5	2.8	2.6	2.0	
Illuminants . . .	4.7	0	1.0	6	0	9	
O ₂ . . .	1.6	0	0	2	2	2	
CO . . .	6.9	12.3	10.8	12.7	13.1	10.6	
CH ₄ . . .	31.1	9	2.4	1.2	2.8	2.9	
H ₂ . . .	36.9	12.5	17.6	19.1	12.9	17.5	
N ₂ . . .	12.5	56.5	50.1	48.4	52.9	52.0	
Temperature °F. . .	2100	2135	2170	2080	2100		
Air							
Ratio . . .	2.25	1.98	1.90	2.40	1.86		
Gas							
Sum oxidizing agents							
CO ₂ , H ₂ O, O ₂ . . .	17.8	18.1	17.7	18.3	16.1		
Sum reducing agents,							
H ₂ , CO, illuminants,							
CH ₄ . . .	25.7	31.8	33.9	27.8	31.9		
Reducing agents . . .							
Ratio . . .	1.45	1.76	1.91	1.52	1.98		
Oxidizing agents							

CO₂ present. With products from the incomplete combustion of illuminating gas that contain small amounts of hydrocarbons and material amounts of hydrogen, conditions seem much more favorable.

Effect of Heating High Carbon Steel in Neutral Atmosphere.—The steel wire used in these tests contained 1.25% carbon and was 0.014" in diameter. When heated to 2,000-2,200° F. for one hour, under conditions similar to those used for the soft iron wire, it was found that oxidation of the metal could be prevented, as with the soft iron wire, but that decarburization could not be prevented. In every experiment at these high temperatures, practically all of the carbon was removed from the metal. This would mean that the decarburization, after one hour at this temperature, had progressed at least 0.007" from the surface. This is not altogether unexpected, since hydrogen as well as carbon dioxide and steam acts as a de-

TABLE III.—EXTENT OF OXIDATION OF FINE IRON AND STEEL WIRES WHEN HEATED TO 2,200° F. IN NEARLY NEUTRAL ATMOSPHERE.

A—Tests with Iron Wire 0.005 inches Diameter and containing 0.04% Carbon.									
Test No.	Weight of wire in grams.		Per cent increase in weight.	of Fe changed to Fe ₂ O ₃ .	Depth of scale in ins.	Ratio Air-Gas.	Mean temp. °F.	Time of heating.	Color of flame at top of muffle.
	Before.	After.							
3.	0.3075	0.4200	36.5	95.5	0.002	2.5	2228	1 hr.	Colorless flame
4.	0.3060	0.3645	19.1	50.0	0.00073	2.43	2100	25 min.	Colorless flame
10.	0.3010	0.3655	21.4	56.0	0.00084	2.40	3080	1 hr.	Colorless flame
5.	0.3050	0.3520	15.4	40.3	0.00057	2.25	2100	1 hr.	Colorless flame
11.	0.2995	0.3350	11.8	30.9	0.00043	2.20	2090	1 hr. 15 min.	Slightly colored
8.	0.3060	0.3320	8.5	22.3	0.00029	2.16	2170	2 hrs.	Slightly colored
7.	0.3045	0.3105	2.0	5.23	0.00005	2.08	2170	2 hrs.	Slightly colored
6.	0.3175	0.3185	0.3	0.78	0.00001	1.98	2135	45 min.	Yellow flame
9.	0.3116	0.3073	1.2	3.14	0.00004	1.87	2220	1 hr.	Yellow flame
12.	0.2997	0.3007	0.3	0.78	0.00001	1.86	2100	1 hr.	Yellow flame
B—Tests with Steel Wire 0.014 inch Diameter and containing 1.25% Carbon.									
11.	0.2335	0.3017	27.9	10.60	0.00038	2.40	2080	1 hr.	Colorless flame
15.	0.2995	0.3035	1.33	6.76	0.00029	2.20	2090	1 hr.	Slightly colored
13.	0.3745	0.3713	0.0	3.28	0.00012	1.87	2220	1 hr.	Yellow flame
16.	0.3073	0.3065	-0.26	2.60	0.0001	1.86	2100	1 hr.	Yellow flame

carburizing agent. The rate of decarburizing would certainly be slower in this gas than in ordinary furnace operation, and by the use of still smaller amounts of air decarburization might be altogether prevented, since case-hardening may be produced when pure illuminating gas is used. There should be no difficulty in preventing decarburization at the temperatures used in heat treatment of steel. The details of the test on steel wire are given in Part B of Table III.

SUMMARY.

It has been shown that it is entirely possible to heat iron and steel in an internally fired muffle, even to forging temperature, without any oxidation or formation of scale on the surface of the metal. A neutral atmosphere is produced when approximately one volume of illuminating gas is combined with two volumes of air; a mixture so rich that it will not burn unless preheated. This atmosphere, although neutral to iron, decarburizes steel slowly at forging temperatures; but it is a much less active decarburizing agent at this temperature than the ordinary furnace atmosphere, and may be rendered still less active by using a mixture richer in gas. At the temperatures used in heat treatment, gas of this composition would have a decarburizing action.

It should be feasible to make a commercial application of this process. The heat evolved by the primary combustion within the muffle is about 27% of the possible total heat, and is sufficient to give a theoretical combustion temperature of 2,200° F., starting with cold gas and cold air. A secondary combustion around the muffle aids in keeping up the temperature so that there is no trouble in actually realizing 2,200° in a muffle. This secondary combustion liberates all the heat units in the gas, and so raises the thermal efficiency. If the sensible heat of the waste gases was used to preheat the entering air, a high efficiency could be obtained. When starting with a cold furnace, the full amount of air for complete combustion could be introduced within the empty muffle, which could thus be quickly brought to working temperature. The primary air supply could then be reduced to the desired quantity, and the metal introduced into the muffle, where, exposed to the neutral gases, it would be more rapidly heated than in an externally heated muffle, and would be protected from oxidation. The saving in metal should be considerable, and would probably compensate for any increase in the cost of fuel. The process presents attractive possibilities in its application to the automobile industry and other industries where quality is paramount.

The gross profits of the Fried. Krupp Steel Works, Essen, Germany, for the fiscal year ended June 30, 1915, were 113,229,821 marks against 54,004,571 marks for the fiscal year ended June 30, 1914. The net profit was 86,465,611 marks against 33,904,224 marks a year ago.

THE DETERMINATION OF BENZOL IN GAS MIXTURES.*

By G. A. BURRELL and I. W. ROBERTSON.

With the present great demand for benzol and the installation of plants at different places for obtaining this constituent, there has arisen a demand for a rapid method of determining the benzol content of gas mixtures. Hence a scheme follows which the authors have used in determining it in the carbureted mixed coal and water gas of Pittsburgh. Fig. 1 illustrates the apparatus. The bulb contains phosphorus pentoxide for removing water vapor. To start a determination the apparatus is connected to a vacuum pump and exhausted of its air; a Gerky pump will do. The gas mixture is then introduced at atmospheric pressure, the barometer read, and the two bulbs immersed in a mixture¹ of solid carbon dioxide and acetone or alcohol. After waiting about 10 minutes, as much gas as possible is withdrawn from the bulbs by means of the vacuum pump. The gases removed will be those of high vapor pressure at -78° C. In the case of the mixed coal and water gas the authors worked with, they are CO₂, O₂, CO, H₂, CH₄, N₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈ and C₄H₈; in fact, practically all the gases except the benzol. Next the stopcock on the apparatus is closed, the cooling mixture removed, and the benzol allowed to vaporize at room temperature. Its pressure is then read on the side-arm mercury manom-



Fig. 1.

Sample No.	1	2
Original pressure of gas ...	744 mm.	744 mm.
Partial pressure of benzol vapor	10 mm.	9 mm.
Percentage of Benzol....	$\frac{10 \times 100}{744} = 1.34$	$\frac{9 \times 100}{744} = 1.31$

eter attached to the apparatus. This pressure compared with the atmospheric pressure gives the percentage of benzol in the gas mixture. The results of two determinations are shown in Table I.

To obtain other data on this method of separation, the distillate from the above freezing process was next passed into fuming sulphuric acid. In the case of Sample No. 1 there was obtained 7.32 per cent of illuminants, and in the case of Sample No. 2, 7.39 per cent. The total illuminants in the Pittsburgh gas, as

*From The Journal of Industrial and Engineering Chemistry, in which it is published with the permission of the Director of the Bureau of Mines.

¹This mixture gives a temperature of about -78° C. The solid carbon dioxide, obtained by releasing the gas from a commercial cylinder, through a cloth towel, is mixed with acetone or alcohol to the consistency of slush.

found by absorption in fuming sulphuric acid, is 8.67 per cent. In other words, the benzol percentages as found when added to 7.32 and 7.39, respectively, equal 8.66 and 8.70 per cent, or almost identically the same quantities as the total illuminants in the coal gas.

Benzene reacts with oxygen as follows:



The contraction is 2.5 volumes and the carbon dioxide is 6 volumes. Table II shows the results of analysis of the residual vapor that was held in the liquefaction bulb (Fig. 1) when the coal gas was cooled at a temperature of $-78^\circ C$. Before analysis the benzol was diluted with air.

TABLE II—ANALYSIS OF BENZOL VAPOR.

	Cc.
Volume taken for analysis.....	28.29
Oxygen added	51.94
Total volume	80.23
Volume after burning.....	75.47
Contraction due to burning.....	4.76
Volume after KOH absorption.....	64.25
Carbon dioxide produced by burning.....	11.42

It will be observed that the ratio of the carbon dioxide to the contraction is almost exactly 6:2.5, showing that the vapor obtained in the benzol determination was principally benzol. Traces of other easily condensable vapors may have been present but apparently in such small quantities as to be negligible.

The authors were unable to find, in the literature, the vapor pressure of benzol at $-78^\circ C$., but apparently it is very small. Benzol boils at $80.12^\circ C$.; at -20° the vapor pressure is 5.76 mm.² The authors prepared saturated vapors of benzol by shaking the pure liquid with air. It was a simple matter to prepare unsaturated vapor by merely diluting the saturated vapor with air. The percentage of benzol was checked by combustion analysis. It was found that all of the benzol could be separated at $-78^\circ C$.

The above tests show that as far as the Pittsburgh gas is concerned the method is satisfactory.

In extracting benzol from coke-oven gases (large-scale operations for this purpose are in progress), the gas is washed with a petroleum distillate, in which the benzol is dissolved, also toluol and other products. As a check on the efficiency of the scrubbing apparatus there is needed a rapid test for the benzol, etc. In this case, toluol or other easily condensable hydrocarbons would interfere with the test, as the vapor pressure of toluol is only 0.0058 mm. at $-78^\circ C$.³ The best one could do would be to estimate them together, along with any other vapors that might also be retained, so that the test would give the efficiency of absorption of all the easily condensable vapors in the scrubbing oil. The authors have made no experiments with coke-oven gas.

Acknowledgment is made to Dr. G. A. Hulett, consulting chemist to the Bureau of Mines, for suggesting this scheme of analysis.

²Landolt and Börnstein Tables, 1905, p. 143, according to Regnault.

³Landolt and Börnstein Tables, 1912, p. 334; according to Barker.

THE IODIDE METHOD APPLIED TO THE DETERMINATION OF COPPER IN THE PRESENCE OF TIN.*

By ROBERT W. COLTMAN.

In the determination of copper in a copper-tin alloy, the usual procedures involve a separation of the copper and tin. The most common method is to decompose the alloy with nitric acid, whereby metastannic acid and copper nitrate are formed. The tin precipitate is filtered off, and the copper determined in the filtrate. This method has the disadvantage that the metastannic acid filters with difficulty; furthermore, the tin precipitate always contains traces of other metals present in the alloy, so that it must undergo further treatment.

Tin and copper may also be separated by sodium sulphide in alkaline solution, whereby the copper separates as sulphide and the tin goes into solution as a sulpho-salt. The inconvenience of this method needs no comment.

Having had occasion to investigate the behavior of metallic copper and metallic tin when treated with concentrated sulphuric acid, the writer was struck by the facility with which the tin was held in solution. The fact that tin goes into solution as a stannic salt when treated with concentrated sulphuric acid is made use of in Low's method for antimony in babbitt metal;¹ the hydrochloric acid added after the decomposition of the alloy ensures the tin and antimony remaining in solution after dilution. It was found that the solution of tin in sulphuric acid alone was fairly stable, and with the knowledge that stannic salts do not liberate iodine from a solution of potassium iodide, the question naturally arose as to whether copper might not be determined by the iodide method in a solution containing tin. Further experiments showed that this was quite feasible; by proper treatment of the alloy a solution of stannic and cupric sulphate in sulphuric acid may be obtained that may be titrated for copper with the same accuracy as a copper sulphate solution alone.

Although hydrochloric acid holds tin in solution much more readily than sulphuric acid, its use was not considered, as copper is not readily soluble in hydrochloric acid and thus would necessitate the use of aqua regia to effect solution of the alloy. The nitric acid would then have to be removed by repeated evaporations with hydrochloric, consuming much time, and making the method much less simple than in its present form.

Preliminary work showed that the best method of preparing the solution was to treat the finely divided alloy with nitric acid until decomposed, and then fume with sulphuric acid over an open flame (using a Jena Erlenmeyer). The metastannic acid dissolves to

*From The Journal of Industrial and Engineering Chemistry. J. Am. Chem. Soc., 23 (1907), 66.

stannic sulphate, and the copper nitrate is converted into copper sulphate. On taking the cold residue up with water, a clear solution is obtained that may be titrated directly for copper by the iodide method.

The use of sulphuric acid alone to decompose the alloy is not satisfactory, as a small residue of copper remains even after repeated fuming. A large excess of acid must be used, otherwise the pasty mass will spatter. It is practically impossible to control the amount of free sulphuric acid present, and this is important, as in using a mineral acid in the copper iodide method, the acidity must be low.

The allowable amount of tin present under given conditions of acidity was determined as follows:

The volume of the solution to be titrated having been chosen as 75 c.c., and the amount of concentrated sulphuric acid as 3 c.c., increasing quantities of metallic tin were dissolved in nitric acid, evaporated with 3 c.c. of concentrated sulphuric,¹ diluted to 75 c.c., and the stabilities of the different solutions compared.

Tin.	Vol.	Conc.	
Gram.	Cc.	H ₂ SO ₄	Remarks.
0.05	75	3	No change in one hour.
0.1	75	3	Slight turbidity in 15 minutes.
0.2	75	3	Would not dissolve to clear solution.

It is evident that not more than 0.1 gram of tin may be present, otherwise hydrolysis and precipitation of stannic hydrate take place in a short time.

The weight of copper titrated may be as high as 0.25 gram ($= \text{---} = 39.3 \text{ c.c. N/10 Na}_2\text{S}_2\text{O}_3$). This weight of copper in the presence of 0.1 gram tin would be equivalent to 71.43 per cent Cu. There would then be 28.57 per cent Sn. As the amount of tin in a bronze is seldom so high as this, there is no danger that the sample taken for analysis will contain more than the allowable weight of tin, provided the amount of copper present is not much over 0.25 gram.

EXPERIMENTAL DATA.

Standardization of Thiosulphate Solution Against Copper Foil.—The sample was dissolved in nitric, fumed with 3 c.c. conc. H₂SO₄, allowed to cool, 25 c.c. water added, and evaporated again to fuming. The solution was allowed to cool, diluted to 75 c.c., 10 c.c. of 40 per cent KI solution added, and titrated with the thiosulphate solution.

No.	Cc.	Grams copper.	Na ₂ S ₂ O ₃ 1 cc. = Grams Cu.
1.....	0.2655	42.37	0.006266
2.....	0.2648	42.24	0.006269
3.....	0.2684	42.83	0.006267
Average value 1 cc. Na ₂ S ₂ O ₃			0.006267

Titration of Copper In Presence of Tin.—The solution was prepared as before, but metallic tin was added to the copper samples:

No.	Weight—Grams	Per cent	Cc.	Cu. Found	Difference
	Cu.	Sn.	Cu.	Sn.	Per cent.
1..	0.2526	0.0311	89.04	10.96	40.31 89.04
2..	0.2507	0.0504	83.26	16.74	40.02 83.30 +0.04
3..	0.2455	0.0799	75.45	24.55	39.15 75.41 -0.04

¹Three cubic centimeters of concentrated sulphuric acid is the maximum amount which may be present in the copper iodide method, according to Gooch and Heath, *Z. anorg. Chem.*, 55 (1907), 129.

These differences lie entirely within the limits of error.

ANALYTICAL PROCEDURE.

Weigh out a sample containing not over 0.25 gram copper and boil with 15 c.c. of 2:1 nitric in a 500 c.c. Jena Erlenmeyer provided with a small funnel to prevent loss. When the alloy is thoroughly decomposed, add dilute sulphuric acid equivalent to 3 c.c. of concentrated acid, remove and rinse the funnel, and evaporate over an open flame. As the evaporation progresses, the solution becomes more and more clear. After the nitric acid is all driven off, and the sulphuric begins to fume, the stannic and cupric sulphates suddenly separate out, forming a very characteristic crystalline mass of pearly scales somewhat resembling manganese ammonium phosphate. The flask must be removed from the flame immediately after this crystallization takes place or the mass will spatter. After cooling, take up with about 25 c.c. water, shake until dissolved, and again evaporate just to fuming in order to remove the last traces of lower oxides of nitrogen. Allow to cool, take up with 50 c.c. cold water (the stannic sulphate dissolves more quickly by using less water at first) and when all is in solution, add 25 c.c. more water, 10 c.c. of 40 per cent KI, and titrate immediately with the N/10 thiosulphate. If the alloy contains a small amount of lead, some lead sulphate remains undissolved, and the solution at the end point is yellowish (owing to the lead iodide) instead of the creamy white of cuprous iodide, but the presence of lead has no effect upon the titration, at least in moderate amounts.

A copper-tin alloy containing about 10 per cent of tin and 8 per cent lead analyzed as follows:

No.	Sample Gram.	Na ₂ S ₂ O ₃ Gram.	— Cu. Found — Per cent.	Average Per cent Cu.
1.....	0.3127	39.49	0.2474 (8)	79.14
2.....	0.3227	40.79	0.2556 (3)	79.22
3.....	0.3303	41.70	0.2613 (4)	79.12
4.....	0.3168	39.21	0.2457 (4)	79.06
5.....	0.3327	42.02	0.2633 (4)	79.15

In the analyses indicated as 4 and 5 above, the alloy was decomposed with nitric, the metastannic acid filtered off, and the copper determined in the filtrate after evaporation with sulphuric.

Too much stress cannot be laid upon the fact that a second fuming of the solution is necessary: 0.05 gram of metallic tin, treated with nitric, fumed *once* with sulphuric, and diluted to 75 c.c., gave a blue color with KI and starch requiring 0.55 c.c. to discharge it. When this same amount of tin was fumed twice, potassium iodide and starch gave no color in the diluted solution.

As regards the time necessary, determinations 1, 2 and 3, cited above, were run in one hour. The filtering, washing and evaporating necessary when the ordinary method was used, made the time about five hours. (In this, no correction was made for any copper remaining with the metastannic acid.)

The method proposed is simple, accurate, and rapid:

the advantages of carrying out the analysis in the same container are obvious.

In conclusion, it must be remembered that no metals which separate iodine from potassium iodide may be present, such as antimonite or ferric salts; the method has naturally the limitations of the iodide method in this respect. It is simply the desire of the writer to show an extended use of this excellent method, thus making it available under apparently adverse conditions.

TITRATION OF NITRATES WITH FERROUS SULPHATE.*

By FRED C. BOWMAN and W. W. SCOTT.

The great variety of methods of determining nitrates found in chemical literature shows the need felt by chemists for simpler ways of making this important analysis. Most methods now in use involve distillation or evaporation or the use of special apparatus, all of which take a good deal of time and attention.

The method proposed by the authors is as easy and quick as any ordinary titration, has a wide range of usefulness and is accurate enough for most purposes.

BIBLIOGRAPHY.

The first mention of the method was made by Grossart¹ in 1847. He titrated nitrates in boiling 60 per cent sulphuric acid with a ferrous sulphate solution, using ferricyanide as an outside indicator. He gives no details or test analyses. No doubt his results were less accurate than he thought.

Mohr² announced the discovery of the method in 1861. He dissolved the sample in sulphuric acid (diluted 1 to 9) and titrated at 70° to 80° C. with a ferrous sulphate solution containing 200 grams of the salt per liter, using as the end point the appearance of a brownish color. He declared that it was a good technical method, but Fresenius³ and Eder,⁴ who examined it later, condemned it strongly.

In 1809 van Deventer⁵ carried out the reaction over mercury in a Crum tube with exclusion of air, using fairly strong sulphuric acid as a medium and a weak ferrous sulphate solution as reagent. The process was awkward to handle.

No comment on these methods was found in the journals, and evidently they failed of acceptance. They were all based on the reduction of the nitrate to NO and not to N₂O₃, as in the method given below, for estimations in presence of sulphuric acid. No mention of acids other than sulphuric was found in the literature.

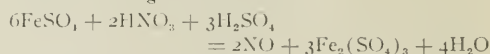
ESTIMATION OF NITRIC ACID IN PRESENCE OF ARSENIC ACID.

The writers devised the method given below, origi-

inally, for the purpose of estimating nitric acid in arsenic acid. The original form of the method was as follows:

Dilute the sample to be tested to 100 c.c. with nitre-free arsenic acid of such strength that there is not more than 20 per cent water in the mixture. Then titrate with a ferrous sulphate solution, containing 264.7 grams FeSO₄·7H₂O and 50 c.c. strong sulphuric acid per liter (1 c.c. = 0.02 g. HNO₃). Standardize the solution on a known amount of nitric acid.

The following reaction occurs:



The ferrous sulphate forms a dark brown color, which disappears on stirring as long as any nitric acid remains. The end point is the first permanent brown and is readable to 0.03 c.c. During the first two-thirds of the titration, the ferrous sulphate is taken up very quickly; then a lively evolution of NO commences and continues to the end. It would be thought that the oxygen of the air might reoxidize the NO and cause error in the titration, but this does not occur.

The presence of too much water in the solution makes the reaction "hang," i. e., refuse to begin. If the solution is warmed with a few c.c. of the ferrous sulphate solution, the reaction begins abruptly and runs easily thereafter. Heating even to boiling does not change the reaction, but may volatilize some of the HNO₃. There should not be more than 25 per cent of water present at the end of the titration. Water added in the ferrous sulphate solution must be taken into account.

In the light of subsequent knowledge, it would seem better to make up the standard solution without any sulphuric acid. The proportion of sulphuric acid present in a titration was, however, so small that its influence could not be detected.

A few analyses will show the accuracy of the method.

Per Cent HNO₃ in Arsenic Acid.
Nitrometer..... 0.25 Ferrous sulphate method... 0.27
Nitric acid was added to nitre-free arsenic acid and the mixture analyzed:

Grams nitric acid.	(1)	(2)	(3)
Taken	0.6610	0.5968	0.0661
Found	0.6608	0.5984	0.0660

A small excess of ferrous sulphate is necessary to give a good color at the end point. Usually, this does not amount to more than 0.1 c.c., but for small quantities of nitrates the correction is greater. In this case a little nitric acid should first be added to the arsenic acid and titrated with ferrous sulphate to a brown tin; then the sample to be tested may be added and titrated accurately.

ESTIMATION OF NITRIC ACID IN PRESENCE OF PHOSPHORIC ACID.

The same reaction between ferrous salts and nitrates occurs in phosphoric as in arsenic acid, but titrations are even more satisfactory. No heating is required to start the action and the end point is a little

*From The Journal of Industrial and Engineering Chemistry, Vol. 1, p. 100, 1909.
†Sur un nouveau dosage de l'acide azotique et des azotates, Grossart, Compt. rend., 1 (1847), 21.

‡Dinsler's Polytechnisches Journal, 160 (1861), 219.

§Zeitschrift für anal. Chemie, 1 (1862), 32.

¶Ibid., 16 (1877), 267.

‡Zeitschrift für physik. Chemie, 21 (1899), 50.

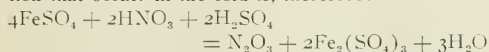
sharper than in arsenic acid, being readable to about 0.02 c.c. with the ferrous sulphate solution described above. Practically no excess is required at the end point, except for very small amounts of nitrate. As with arsenic acid, the concentration of water present at the end of a titration should be less than 25 per cent and better results will be obtained with 20 per cent.

Below are a few test analyses made in phosphoric acid:

Grams HNO ₃	(1)	(2)	(3)
Taken	0.6610	0.5968	0.5968
Found	0.6618	0.5984	0.5966

ESTIMATION OF NITRIC ACID IN PRESENCE OF SULPHURIC ACID.

Both arsenic and phosphoric acids have the drawback that they are too expensive for general use in titrations. Sulphuric acid is the only strong acid available in the laboratory at a reasonable price. When this was tried the surprising fact was discovered that the reaction proceeds only two-thirds as far as in arsenic and phosphoric acids. Nitrates are reduced, not to NO, but to N₂O₃. Strong heating will, however, drive the reaction somewhat further. The reaction that occurs in the cold is, therefore:



The end point is a delicate pinkish brown, not so sharp as with the other acids, but as easy to read as the usual methyl orange end point in acid titrations.

Effect of Water.—Experiments show that water slows down the reaction and weakens the color of the end point, so that a considerable excess of ferrous sulphate is required to give a readable tint. Larger quantities of water stop the reaction entirely in the cold.

Per cent water at end point—	15.	20.	25.	25.	35.
Gram HNO ₃ taken.....	0.4963	0.4963	0.4963	0.4963	0.5968
Gram HNO ₃ found.....	0.4935	0.4923	0.5024	0.4973	0.6808

These figures are not of high accuracy, but they show that 25 per cent of water is permissible as a maximum, though it makes a rather difficult end point.

Effect of Temperature.—The temperature of titration should be low. Too high a temperature acts in two opposite ways: (1) it causes volatilization of HNO₃, which leads to low results; (2) it causes a slight reduction of N₂O₃ to NO, which makes for high values.

Maximum temperature during titration—	40° C.	50° C.	60° C.	90° C.	110° C.
Gram HNO ₃ taken.....	0.4963	0.4963	0.4963	0.4963	0.4963
Gram HNO ₃ found.....	0.4960	0.4947	0.4940	0.5038	0.5460

The lowest temperature gives the best results; at medium temperatures the compensation of errors is fair but irregular; at high temperatures the results are high and the end point is very bad. The conclusion is that the temperature should be kept as low as possible, and should not exceed 60° C. So much heat is generated by running the ferrous sulphate solution into the sulphuric acid that the test beaker must be cooled in a bath of water during titration.

Correction for End Point.—It was found that ferrous sulphate attacks N₂O₃ slowly under the conditions of the titration, but that it has so marked a preference for HNO₃ that no reduction of N₂O₃ occurs while HNO₃ is present. As the brown color of the end point is due to the formation of a compound of FeSO₄ and NO, some slight reduction to NO must occur always. The results of many experiments show that about 0.2 c.c. excess of ferrous sulphate solution (1 c.c. = 0.02 g. HNO₃) is required to give the brown tint of the end point in a volume of 100–150 c.c. This holds for titrations ranging from 0.5 c.c. to at least 80 c.c.

Effect of Commonly Occurring Impurities.—The effect of impurities ordinarily occurring in nitrates was investigated by adding them to a known amount of nitric acid and titrating the latter. The table at the top of p. 768 gives the results.

The table shows that nitrite has little effect; chloride, iodide and bromide cause low results in quantities as little as 2 per cent, and chlorate, bromate and iodate cause high results. Elsewhere in this paper it is shown that ammonium salts have no effect.

INFLUENCE OF SALTS ON FERROUS SULPHATE TITRATION FOR NO₃ IN PRESENCE OF SULPHURIC ACID.

Amount of HNO ₃ taken, 0.3039 g.		Salts Added to HNO ₃ Titration.		Per cent of Cc.	Remarks.
Formula.	Weight Gram.	mixture tested.	FeSO ₄ solution.		
Blank	None		15.8		
KNO ₃	0.08511	21.9	15.71		
KNO ₂	0.4256	58.6	16.06		
KNO ₂	0.8511	73.0	16.76		Odor of N ₂ O ₃ evident
NaCl	0.05846	16.0	14.96		
NaCl	0.2923	49.0			No distinct end point
NaCl	0.00585	1.9	15.65		
KI	0.166	33.2	11.4		
KI	0.017	5.3	15.25		
KI	0.0017	0.57	15.8		
KBr	0.1190	28.0			No distinct end point
KBr	0.0119	3.8	15.66		
KClO ₃	0.3039	50.0	45.0		No good end point
KIO ₃	0.10701	26.0	17.36		
KIO ₃	0.01070	3.4	15.96		
KBrO ₃	0.0835	21.6			No distinct end point
KBrO ₃	0.00835	2.7	16.06		

PROCEDURE RECOMMENDED.

Based on the foregoing results, the following standard procedure is recommended for the analysis of nitrates with concentrated sulphuric acid as the medium:

Ferrous Sulphate Solution.—Dissolve 176.5 grams FeSO₄·7H₂O in 400 c.c. water. Stir into this gradually 500 c.c. of dilute sulphuric acid, made by mixing equal volumes of water and concentrated acid. Cool the mixture and make up to 1000 c.c. The order of mixing given above should be followed, for a different order is apt to cause precipitation of an iron sulphate that cannot be redissolved.

1 cc. = 0.02 g. HNO₃ and contains 0.8 cc. water.

Standardizing.—Either potassium bichromate or nitric acid^a may serve for a standard. With the

^aPotassium nitrate may be used for standardizing, but it involves more work than the use of nitric acid. To dry a sample of potassium nitrate and test it for impurities, particularly sodium, is more troublesome than to titrate a nitric acid solution. The writers met trouble in using a supposedly pure sample of potassium nitrate for standardizing, and for that reason abandoned it in favor of nitric acid.

former, estimate the strength of the iron solution by Penny's method. Remember to allow 0.2 c.c. for the end point in titrating nitrates.

1 gram $K_2Cr_2O_7 = 0.6426$ g. HNO_3 .

A more satisfactory method of standardizing is to titrate a nitric acid solution of known strength under the exact conditions in which the iron solution is to be used. For this, dilute 41 c.c. of the usual 70 per cent laboratory nitric acid to 1000 c.c. and titrate with normal caustic alkali. Use 10 c.c. of the dilute nitric acid to standardize the ferrous sulphate solution in the manner described above.

A certain solution standardized carefully by both methods gave the following results, showing that the methods agree well:

1 cc. = 0.02068 g. HNO_3 (HNO_3 as standard).

1 cc. = 0.02073 g. HNO_3 ($K_2Cr_2O_7$ as standard).

Titration.—The sample should be chosen to contain 0.3 to 0.6 g. HNO_3 . For the most accurate work, the titration should be on practically the same quantity of HNO_3 as was used in standardizing the solution.

Place 100 c.c. concentrated sulphuric acid, free from nitrates, in a 250 c.c. beaker set in a large porcelain casserole full of cold water. Run the sample in slowly from a 10 c.c. pipette to the bottom of the acid, stirring meanwhile with the pipette; this procedure is designed to prevent loss of nitric acid fumes. Run in the ferrous sulphate solution slowly in a fine stream with constant stirring until the solution turns from yellow to faint brown or pink. Then rinse out the pipette⁷ by sucking it full of the acid and draining it and continue titrating cautiously to the first color change. The end point is clear to 0.05 c.c. and different operators should agree within 0.1 c.c.

The casserole of water serves the double purpose of cooling the acid and making the end point much clearer. It is sometimes necessary to halt the titration and let the solution cool. The temperature should never exceed 60° C. and is better kept below 40° C.

Let the burette stand five minutes before taking the reading, as the ferrous sulphate solution drains very slowly.

SOME INDUSTRIAL APPLICATIONS OF THE METHOD.

Nitric Acid In Oleum (Fuming Sulphuric Acid).—Weigh about 10 grams of the oleum in a pipette and titrate according to the scheme given above. A pipette of known content may be used for routine work, so that weighing is unnecessary. This method does not estimate nitrous acid in the oleum.

The accuracy of the ferrous sulphate method was given a rigid test by two laboratories by analyzing the same lot of samples independently and afterward comparing the results.

PER CENT NITRIC ACID IN OLEUM.					
Analyses.	Method.	I.	II.	III.	IV.
Seller's	$FeSO_4$	2.40	2.82	3.23	3.35
Buyer's	Nitrometer	2.35	2.79	3.26	3.39
Difference		+0.05	+0.03	-0.03	-0.04
Analyses.	Method.	VI.	VII.	VIII.	IX.
Seller's	$FeSO_4$	3.50	3.48	3.57	3.53
Buyer's	Nitrometer	3.53	3.50	3.58	3.57
Difference		-0.03	-0.02	-0.01	-0.04

⁷The pipette used for measuring the sample should be graduated to contain, not to deliver.

The ferrous sulphate method is the quickest and probably the most accurate way of determining nitrates in oleum.

Ammonium Nitrate.—A test on pure salt showed:

Taken..... 0.5000 Gram Found..... 0.5004 Gram

The method has been used extensively in one laboratory for the rapid determination of nitrates in the presence of nitrites and ammonium salts. This would be a laborious analysis by the usual methods.

Sodium and Potassium Nitrates.—Samples of chemically pure potassium nitrate and a sample of commercial nitrate of soda were tested with the following results:

Gr. KNO_3 (1) (2) Commercial $NaNO_3$
Taken.. 0.7000 0.3500 By Devarda's method 97.62 per cent
Found.. 0.6997 0.3510 By $FeSO_4$ method... 97.65 and 99.13

In the latter case the end point was bad, and the impurities present caused poor agreement between duplicates. This method is only roughly correct for impure nitrate of soda.

"Mixed Acid" (Nitric and Sulphuric Acids).—

Samples of mixed acid weighing 6 to 7 grams were diluted to exactly 100 c.c. with concentrated sulphuric acid and 10 c.c. portions were titrated. The ferrous sulphate solution used was only one-half as strong as is recommended above; it was made up by diluting one volume of the standard solution with one volume of 60 per cent sulphuric acid. The temperature of titration was kept down to 70° F. by the use of an ice bath. The acids used were most carefully analyzed by the evaporation method and the ferrous sulphate solution was standardized against a mixed acid of known analysis.

Per Cent HNO_3 —	(1)	(2)	(3)
By $FeSO_4$ method.....	50.32	50.16	49.49
By evaporation method.....	50.15	50.02	49.35

These analyses represent the limit of accuracy attainable by this method. Reasonable care to observe constancy of conditions permits an accuracy of 1 in 300, where large amounts of nitrates are present.

SUMMARY.

I—The authors have devised a method based on the well-known ferrous sulphate test for nitrates, by which large amounts of nitric acid may be titrated directly.

II—The accuracy of the method is shown by analyses of known amounts of nitric acid combined and free, comparison being made with usual standard methods. With care the error does not exceed 1/300 of the quantity of nitric acid estimated. The method is not suitable for traces.

III—Constancy of conditions is important. The water content should not exceed 25 per cent of the sample titrated and the temperature should be kept below 60° C. Chlorates, bromates, iodates, chlorides, bromides and iodides interfere, but nitrites do not when sulphuric acid is used as a medium.

IV—A detailed procedure for analysis is given.

V—Some applications of the method to technical analysis are included; these are now in regular use in several technical laboratories.

The CHEMICAL ENGINEER

HARRY McCORMACK, Editor.

PUBLISHED MONTHLY by the MYRON C. CLARK
PUBLISHING CO.,

608 S. Dearborn Street, Chicago

*Entered as Second Class Matter, Aug. 19, 1907, at the Post Office
at Chicago, Illinois, under Act of March 3, 1879.*

Subscription—United States, Cuba and Mexico \$2.00
Extra postage to Canada 25c a year; to foreign countries 50c a year.
Remittances may be made by check, draft or money order in favor of
THE CHEMICAL ENGINEER

All communications should be sent to THE CHEMICAL ENGINEER, 608
S. Dearborn Street, Chicago, Ill.

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NOTES AND COMMENTS.

Chilean Production of Nitrate.

United States Commercial Attache, V. L. Havens, writing from Santiago, Chile, under date of October 18, 1915, says that the official figures of Chile's production of nitrate during the first three months (July-September) of the current nitrate year place the output at 9,857,282 Spanish quintals (of 101.4 pounds), as compared with 13,408,094 quintals and 15,154,614 quintals in the corresponding periods of 1914-15 and 1913-14, respectively. Exports for the quarter totaled 13,720,479 quintals (against 7,876,625 and 11,980,815 quintals), 6,244,625 quintals of which went to Europe and Egypt (against 4,379,767 and 8,615,977 quintals in the corresponding three months of the two preceding nitrate years, respectively), 6,185,562 to the east coast of the United States (against 2,868,328 and 2,557,808 quintals), and 485,947 quintals to the west coast of the United States (against 238,700 and 242,880 quintals).

Chemical Research and the War.

The report of the editor of Chemical Abstracts for the year 1915, as published in the current number of the Journal of the American Chemical Society, shows pretty clearly the effect of the great war upon chemical research throughout the world. Since 1911 Chemical Abstracts has reviewed and abstracted the world's output of published matter in chemistry. In 1915, 18,440 articles were abstracted. This is only three-quarters (75.8%) of the average number abstracted and published for the three preceding years (24,339).

An increase of about 30 per cent in number of original articles upon pure chemistry published in the Journal of the American Chemical Society in 1915 over the number published the year before (Report of Editor, J. A. C. S., Jan., 1916) indicates a stimulation of American chemical research accompanying the suppression of research in Europe. The great activity in the chemical industries here, caused by the war, is doubtless accompanied by an increased volume of technical research, little of which, however, is likely to be published.

American Company Produces Synthetic Camphor.

The establishment of an American factory for the manufacture of synthetic camphor has been brought to the attention of the Department of Commerce by the officers of the company, who propose to enter a market which has been occupied heretofore by foreign camphor. American consumers have been depending upon importations, which, during the fiscal year ended June, 1915, amounted to 4,899,873 pounds, valued at \$1,421,122. The possibility of developing American manufacture to large proportions is emphasized in communications from the American Camphor Corporation, which is operating a factory in Philadelphia. The new company calls attention to the fact that it is creating a market for turpentine. "To make enough camphor to supply our home industries," it says, "would take over 10,000 barrels of turpentine, as much as is now in store at Savannah, the largest supply market."

Sulphuric Acid In 1915.

The sulphuric acid industry in 1915 presented both remarkable and normal features. In spite of the abnormal demand a great deal of sulphuric acid was consumed in the factories where it was made. The trade in strong acids was much more active on account of the demand for explosives and other war munitions, but this demand came only after the first quarter of the year and was very strong only during the last six months. Before that time some acid plants were shut down. The estimated production of sulphuric acid of 50°, 60°, and 66° strengths in 1915 is 4,007,000 tons, expressed in terms of 50° acid. In addition there was a production of nearly 49,000 tons of fuming acid and oleum. This is an increase of 6½ per cent in the three common grades, but the production of

fuming acid and oleum more than doubled. These figures include by-product acid produced at copper and zinc smelters amounting to 952,000 short tons of 60° acid. Compared with the production of 1914, this is an increase of 25 per cent, or 191,000 tons. The prices per ton of the stronger grades of acid, especially 60°, 66°, and oleum during the last part of the year ranged far above those of 1914, and the total value of the output will therefore be in excess of what it was in that year. The estimates are based on returns to the United States Geological Survey, compiled by W. C. Phalen, from 95 per cent of the producers, and estimates of the remaining 5 per cent. It is believed that the figures are conservative and that they will be increased when complete returns are received.

Huddersfield to Have Great Dye Works.

After carefully considering a number of locations the directors of British Dyes (Ltd.) have decided to establish their works for the production of synthetic dyes at Huddersfield. The purpose of this company is to manufacture dyes on such an extensive scale as to make the dye users of this country independent of foreign supplies. The site selected is a 450-acre tract in the valley of the Colne River adjacent to the works (formerly belonging to Read Holliday & Sons) taken over by British Dyes a few months ago. It is estimated now that the new works will eventually employ 10,000 adults, which means an added population to the city of probably 35,000 people. The great problem for the municipality will be to house so large a number of people. The borough council, the chamber of commerce, and prominent citizens have this matter seriously under consideration at the present time.

French Shell Specifications.

According to The Iron Age one of the French shell specifications puts these chemical limits on the steel: Carbon, 0.34 to 0.42 per cent; manganese, 0.55 to 0.75 per cent; silicon, 0.15 to 0.25 per cent; phosphorus, 0.03 to 0.08 per cent, and sulphur not more than 0.05 per cent. A British high-explosive shell specification puts the manganese limits at 0.4 to 1.0 per cent and fixes maximum limits as follows: Carbon, 0.55 per cent; nickel, 0.5 per cent; silicon, 0.3 per cent; sulphur, 0.05 per cent; phosphorus, 0.05 per cent and copper, 0.1 per cent. In respect to physical qualities, the French specification for the shells demands a steel which will show a tensile strength of 78,210 to 92,430 lbs. per square inch and 18 per cent elongation after heating to 1652° Fahr. and slow cooling and 106,650 to 147,900 lbs. per square inch and 8 per cent elongation after heating to 1562° Fahr., quenching in water and then drawing 15 minutes in a lead bath at 980° Fahr. A British specification for high-explosive shells stipulates steel from ingots from which there has been a 20 per cent discard (as against 40 per cent recently

obtaining) and a yield point of 42,500 lbs. per square inch, a breaking point of 78,000 to 110,000 lbs. and elongation of 17 per cent.

Sulphuric Acid.

The American Fertilizer reports that there is likely to be a steady demand for greater quantities of sulphuric acid in this country, even after the war is over. Expansion of American manufacturing will be permanent. Our home market is growing larger each year and we will hold at least a part of our new-found foreign trade. There are a hundred uses for sulphuric acid, and a well-designed plant built now will be able to write off most of the cost of construction before the war ends and will be in a position to meet competition in the ordinary lines of trade. The fertilizer industry is vitally interested in an abundant supply of sulphuric acid and should encourage an increase of production.

Hardened Filter Paper.

Writing in the Pharmaceutical Journal on a process for toughening ordinary filter paper, Mr. W. R. Rankin states that a substitute for the smooth, hardened filter paper of German make may be prepared by dipping the best English filter paper very quickly in nitric acid (sp. gr. 1.4), draining and washing in running water until most of the acid is removed. The remainder is neutralized by immersion in 0.5 per cent ammonia solution. The paper is afterwards washed thoroughly, pressed and dried at 100° C. When dry, the paper is subjected to the same treatment. Excessive temperatures should be avoided in drying, as the cellulose is nitrated to some extent. A shrinkage of about 10 per cent should be allowed for. An inferior substitute may be got in a single operation by dipping filter paper in a mixture of 65 parts sulphuric acid (sp. gr. 1.84) and 35 parts nitric acid (sp. gr. 1.42).—M.

British Embargo Changes.

The exportation of hematite pig iron and of iron and steel smelting scrap to all destinations is prohibited, and the exportation of the following products to all destinations other than British possessions has been forbidden: Bichromate of soda, bladders, casings and sausage skins, colchicum and its preparations, solid drawn steel tubes, and wireless telegraph apparatus. Material for telegraphs and telephones, vegetable fibers and yarns made therefrom (not including linen yarns at present free from embargo restrictions) may not be exported to countries in Europe.

WANTED—I. C. S. graduate (young), with commercial experience, wants position as assistant chemist; reliable in inorganic analysis. Box 100, The Chemical Engineer.

The Chemical Engineer

PUBLISHED MONTHLY

at 608 S. Dearborn Street, Chicago, Illinois

Vol. XXIII.

CHICAGO, FEBRUARY, 1916.

No. 2.

ADVANCES IN THE FIELD OF CHEMISTRY DURING 1915.*

By HELEN R. HOSMER.†

Science does not always progress by clean and logical steps, and frequently her most fruitful discoveries fail to receive instant recognition. More often her building is in the way of a fragment aimlessly added here and there as fickle fancy may direct to the master picture puzzle which she is slowly piecing, and yet what appears a fragment, now idly cast upon the board, may prove tomorrow the part so necessary for the completion of some half-forgotten design. A review of the events of any one year made before lapse of time has lent perspective can hardly fail to omit important points, and to put unnecessary emphasis upon others. These notes can therefore merely present a few of the occurrences of interest in one or two fields during 1915, and it must be frankly admitted that the choice is undoubtedly biased in favor of those things which are near at hand, and familiar in their details and bearing. The appearance of prejudice is further accentuated by the fact that, as might be expected, the warring nations and their near neighbors are neither in the mood nor condition to forward investigation, and their output of published material has been very much curtailed. It is probable that in Germany, at least, there is much research of an intensive sort in progress which cannot be revealed at present. Rumor has mentioned a number of accomplishments sufficiently startling, such as the manufacture of explosives without cotton, and of an edible flour from sawdust. Details are, however, lacking.

In the field of pure chemistry there have appeared several papers of considerable interest.

Richards¹ has continued his work upon compressibilities by a determination of the values for seven metals, of which two, tantalum and tungsten, had not been previously studied. The compressibility of mercury, which is of especial importance, because it is used as a standard of reference for all other values determined, was re-determined by reference to the new absolute value for iron recently obtained by Bridgman.

Tungsten was found to have the smallest compressibility of any substance yet measured with a value of 0.28×10^{-10} megabars.

In a later paper² is given a general discussion of the degree of accuracy of the determined values for the 38 elements, which have been carefully studied and re-calculated in accordance with the recent very carefully determined value for mercury. The values agree very well with those determined by Grüneisen in accordance with his theory of elasticity. The relation of compressibility to other properties is discussed. The compressibilities of liquids may not be compared with those of solids, since several which have been investigated in the solid, and also in the supercooled condition, have shown a value two or three fold greater in the liquid than in the solid state. For this reason, those elements whose compressibilities have been determined in the former state have been omitted from consideration. Curves plotting compressibilities of the solid elements against atomic weights show a rather close parallelism to the atomic volumes curve, and also to the curves for reciprocals of melting-points and coefficients of expansion which suggests some fundamental relation of the four properties.

A number of generalizations may be deduced.

Compressibility increases as the melting point becomes lower, decreases as the density increases, and is proportional to the atomic volume for only such elements as have at once nearly equal densities and melting temperatures. Substances melting very near the temperature of experimentation have abnormally high compressibilities.

An approximate empirical formula expressing these relations has been attempted, but is only qualitatively correct in its present form. It does, nevertheless, indicate tendencies such as would be predicted from the theory of compressible atoms.

Langmuir³, while continuing work upon the effect of introduced gases upon metal filaments in evacuated bulbs, has developed certain new views in regard to heterogeneous reactions and the phenomena of absorption. Conditions are so simplified at very low pressures by the elimination of subsidiary effects due to convection and conduction of heat, diffusion phe-

*From General Electric Review.

†Research Laboratory, General Electric Company.

¹Richards, T. W., and Bartlett, J. Amer. Chem. Soc. 37, 470-81 (1915).

²Richards, T. W., J. Amer. Chem. Soc. 37, 1643-56 (1915).

³Langmuir, J. Amer. Chem. Soc. 37, 1139-66 (1915).

nomena and secondary reactions due to collisions of molecules, that the behavior of the individual molecule is unmasked, and the atomic and molecular nature of matter becomes constantly more apparent. Application of the statistical method, along lines indicated by the kinetic theory of gases, to the problems of chemistry gives a method of attack offering wonderful opportunities which have as yet been little utilized by the chemist. Advances in this direction have hitherto been mainly due to the physicist, energy relations absorbing the attention of the physical chemist. The work of Strutt on active (atomic) nitrogen, and of J. J. Thomson on positive rays, are examples of recent applications of the statistical method.

Langmuir's work consisted in studying the velocity and nature of reactions between filaments of carbon, molybdenum, platinum, iron, palladium and other metals at various temperatures, and low pressures of oxygen, nitrogen, hydrogen, carbon dioxide, chlorine, bromine, iodine, methane, cyanogen, hydrochloric acid, argon, phosphine, and vapors of mercury, phosphorus pentoxide, sulphur, etc. Combination occurs under suitable conditions between each of these gases and tungsten.

Reactions of four different types are exemplified, i. e., attack on filament by gas, reaction between vapor from filament and gas, catalytic action of filament upon gas, and reactions due to electrical discharges through the gas. The data from these experiments afforded material for a study of the mechanism of reaction and nature of products for each individual case, as well as evidence for certain general deductions.

Previous experiment on the electron emission from heated tungsten wires in high vacuum have pointed very directly to the existence upon the surface of the metal of a layer of gas one molecule deep. This evidence has been strikingly corroborated in this later investigation. The rate of reaction seems to be limited, not by the rate of diffusion through an adsorbed layer, but the rate at which the metal becomes exposed by the evaporation of single molecules. In certain cases, as that of carbon and oxygen, the adsorbed layer appears to be chemically combined, and extremely stable. Always the velocity of reaction depends upon the rate at which the molecules involved come into contact with each other, and so involves all such physical factors as affect this latter action, such as the rate at which gas molecules may collide with each other or strike that part of a filament which is in condition to react.

For the only cases in which such purely physical factors were not involved, the temperature coefficient of velocity was strongly negative. The positive coefficient of the other cases was due to the increase in rate of evaporation of filaments, or adsorbed materials with temperature, a physical factor of sufficient magnitude to mask the probably negative coefficient of the true reaction. There is a reason to believe that

the same principles apply to reactions at high pressures, and between solids and liquids.

A study of the merits and practicability of cobalt plating, made by Kalmus, Harper and Savell¹, has yielded interesting results. Cobalt offers a number of very considerable advantages over nickel, not only in regard to the properties of the plate produced, but also because the nature of its salts facilitates the processes of production.

The greater solubility of cobalt metal renders unnecessary the presence of iron in the anode, and the plate produced is therefore purer. This is probably one reason for the better resistance to corrosion which it exhibits. The greater solubility of its salts makes it possible to use more concentrated baths, and, further, in all cases tested, the cobalt solutions have had a higher conductivity than the corresponding solutions of nickel. These facts make possible a much more rapid deposition of metal, and to this saving in time is added the consequent advantage of much increased hardness of the plate.

Comparative tests were made with a series of salts, of both cobalt and nickel, and these advantages were found to hold for almost all in a greater or less degree. The two best solutions of those tested were a cobalt ammonium sulphate, and a cobalt sulphate containing sodium chloride and boric acid. Plates made from these solutions, under conditions identical with those existing in nickel-plating practice, are satisfactory in every way, and can be obtained in one-fourth and one-fifteenth the times respectively required by the fastest satisfactory nickel solutions.

With the second solution, a plate capable of withstanding the usual commercial tests for nickel plate can be deposited in one minute, against one hour required for nickel. The weight of metal used is about one-fourth that of nickel. Massive deposits are also far superior to those of nickel, as there is less tendency to distortion, and the detail is hard, sharp and tough. Tests under commercial conditions indicate the possibility of great economy in methods of production, and have shown that the product is decidedly superior to nickel in wearing qualities.

The production of zinc electrolytically is an advance of especial importance to the metallurgical industry and one first coming into prominence during 1915. The application of this method has been very rapid and plants requiring 10,000 kilowatts for operation are already installed or under contract. There is already in sight further development which will take 303,000 kilowatts more and the expectations of the next five years reach 100,000 to 150,000 kilowatts. The power requirement per ton of zinc is from 150 to 160 kilowatts.

The rapidly increasing use of gasoline as fuel for internal combustion engines, with the consequent increase in price, has given a special interest to the investigation of new sources and methods of producing

¹Kalmus, Harper, Savell, J. Ind. Eng. Chem. 7, 379-98 (1915).

it by the breaking down of more complex hydrocarbons.

Rittman⁵ has studied the decomposition of petroleum with the idea of defining the conditions and character of the so-called "cracking" reactions long applied to petroleum. With this accomplished he has experimented with cracking in the vapor phase, which offers considerable advantages both in ease and safety of operation, and in the nature of the products. Applying the method to some of the less commercially valuable oils which were lacking in low boiling constituents, he found it possible to produce, with proper temperature and pressure regulation, something like a 16 per cent increase in the gasoline yield from an oil ordinarily giving upon distillation about 5 per cent. He also found that with higher temperatures it was possible to increase the content of aromatic hydrocarbons by about 8 per cent.

These results seem to indicate the possibility of so handling cheap oils as to obtain from them products of considerable value either as fuel or in the manufacture of dyes and other coal tar products.

McAfee⁶ has published the details of his process for splitting high boiling petroleum oils into low boiling oils by distillation in the presence of aluminum chloride as a catalyzer. This substitutes for the dangerous and unsatisfactory cracking processes a method by which, with proper adjustment of the condenser temperature, high boiling oils containing unsaturated compounds can be broken down into clear, white, non-offensive, saturated products. The reaction takes place at ordinary pressures, and there is little gas given off, or carbon deposited. The process may be regulated to produce greater or smaller proportions of gasoline. In practice it is so adjusted as to leave the paraffins and lubricating oils after removing the gas oil friction as low boiling hydrocarbons.

TECHNICAL ADVANCES.

Applied chemistry has undergone a very considerable territorial expansion during the year and a half since the outbreak of war with its attendant cutting off of supplies of many materials essential to industry. Germany, with her wonderful co-ordination between education, science, industry, and the state had all too easily monopolized certain lines of production whose vital importance to whole industries, and even to national well being has been sharply revealed in ways that the most indifferent cannot fail to read. The inception of such industries in countries where they have not previously existed constitutes a very real advance in the interests of humanity.

It is of interest then to note a few of the respects in which it is to be hoped that America in the near future may again declare her independence of Europe.

Among the most insistent cries for help that followed the closing of German ports was that of the textile⁷ manufacturers, who saw approaching disaster

in the cutting off of the 85 per cent¹⁰ of their dye materials which had come from abroad. This very real danger seems now to have been warded off by the prompt response of chemical manufacturers, both in the way of extension of existing factories, and the establishing of new. Within a year the American production of synthetic dyes has been nearly trebled, and the output of natural dyes greatly extended. By rigid economy in the use of materials, it will probably be possible to weather the present crisis. With careful attention to the details of manufacture and organization, it is possible that another five years may see America producing the bulk of its own consumption in artificial dyestuffs.

Toluol, benzol, and aniline, necessary intermediates for dye manufacture, are being put out by the Standard Oil Company, the Benzol Products Company and other concerns, in large quantities. Edison, within a few months after the outbreak of war, had in operation a plant for making synthetic phenol and aniline on a large scale. He is now turning out 6,000 lbs. per day of the latter.

Laboratory porcelain and glassware adapted to specific purposes is being put on the market by various producers. The merit of some of these products may yet need confirmation, but the idea is started, and research can accomplish the rest. England,¹¹ who found herself especially hard hit in this regard, has also made a beginning at producing her own, by investigating and publishing the formulae for glasses suited to various uses. Optical glass is also being made in America for the first time. It is expected that Bausch & Lomb will hereafter be able to supply our needs without recourse to importation.

America has long been dependent upon Germany for the supply of all its potash, and the situation would have already become very serious, were it not for the large quantities held in storage at the beginning of the war. A small supply should be available shortly from the treatment of Utah alunite. A plant¹² is nearly completed, which is expected to produce 20 tons of potassium sulphate per day. Processes¹³ have also been worked out for the extraction of potash salts from the Searles Lake brines, and plants designed to produce 100 tons daily are under construction. These should be in operation early this year. Experimental work is also being done upon the utilization of the kelps of the Pacific Coast.

Another substance, of importance in the manufacture of war munitions, for which the world has depended largely on Germany in the past, is the metal magnesium. A process of production has been worked up by Mr. Dantszen of the Research Laboratory, and has been in operation on a small, but increasing commercial scale, for nearly six months. There seems to be an important future for this metal as a constitu-

⁵Rittman, J., *J. Ind. Chem.* 7, 945-53 (1915).

⁶McAfee, J., *J. Ind. Chem.* 7, 737-41 (1915).

⁷Norton, *Scientific American*, Nov. 6, 1915.

¹⁰Little, Address before U. S. Chamber of Commerce, Feb. 6, 1915.

¹¹Nature, 95, 192-3 (1915).

¹²Beckman, *Met. Chem. Eng.* 13, 582 (1915).

¹³Eng. Min. J. 100, 936 (1915).

ent of light alloys, and there is no doubt that America will be able to economically supply her own demand even against foreign competition.

Probably not the least valuable of the advances in applied chemistry is the impetus to effort given by the clear demonstration, staged, to our good fortune, across the water, of the fact that systematic study rather than genius brings the solution of the problems of existence, and research in one form or another is the key to evolution in the human race.

DYESTUFF SITUATION IN THE UNITED STATES AT THE CLOSE OF 1915.*

By THOMAS H. NORTON.†

When the great world conflict broke out, Aug. 1, 1914, the status of the artificial dyestuff industry in this country was as follows: Six factories, employing at the utmost 400 operatives, were manufacturing coal-tar colors to the extent of 3,300 short tons annually. Imports from Europe amounted to 25,700 short tons annually. Of this quantity, German manufacturers contributed 22,000 tons. The total annual consumption of synthetic colors in the United States was about 29,000 short tons.

The industries in this country most vitally dependent upon artificial colors are the following:

Industries.	Establishments.	Employees.	Capital.	Value of Product.
Textile	5,353	915,858	\$1,841,242,131	\$1,634,636,490
Leather	5,728	309,766	659,231,312	992,713,322
Paper	2,439	145,711	527,537,821	541,736,820
Paint and varnish	791	14,210	103,994,908	124,889,422
Ink	118	1,626	9,257,817	11,370,918
Total	14,429	1,387,901	\$3,141,263,989	\$3,229,346,981

In addition to the above there come a multitude of minor industries—feathers, furs, straw work, wood-work, shoe dressing, etc. It has been estimated that over 2,000,000 working men and working women are occupied in industries which are directly dependent upon the use of artificial colors.

If to these be added the host of industries involving the use of colored wares—the printers, painters, tailors, dressmakers, milliners, etc.—it is easily seen that a large share of the population of the United States, occupied in gainful pursuits, is directly or indirectly dependent upon regular supplies of dyestuffs.

The general public, the ultimate consumers of manufactured articles, are naturally very seriously affected by any crisis which interferes with the normal supply of coloring materials.

The reflex action of the tremendous struggle across the ocean is evident in every phase of our national life, and especially in the field of industrial effort. It can, however, be easily realized from the above statement that in no section of this field has the influence of trans-Atlantic conditions produced such momentous

results as in the manufacture and consumption of artificial colors.

The changes which have occurred since August 1, 1914, may be summarized as follows:

At the outbreak of the war the textile and other allied interests of the United States were threatened by a shortage in the supply of dyestuffs. For some weeks shipments were entirely suspended. Gradually, as the result of the most strenuous efforts on the part of leading representatives of the textile industries and of the firms engaged in importing artificial colors of foreign origin, the movement was restored to nearly normal figures. The possibility of a complete cessation in shipments was, however, constantly present as a menace, hanging like the sword of Damocles over the head of every consumer of synthetic dyes. The threatened danger arrived eight months ago, when an embargo on the shipment of dyes of German origin to neutral countries came into effect. Since March 15th no wares in this category have been received. During nearly all of this period there has been in force a permit issued by the British Government allowing free passage to the United States of two steamer loads of artificial colors of German origin. Thus far the German Government has steadily refused to allow this supply to pass out of the Empire, unless a *quid pro quo* were accorded in the form of a shipment from the United States to Germany of an equivalent amount of cotton or of nitric acid.

This deadlock still exists. During the last eight months small quantities of coal-tar dyes of Swiss origin have reached the United States. The amount has been very limited, but it has been most welcome.

On Feb. 20, 1915, pursuant to a resolution of the Senate, a full report on every phase of the dyestuff situation was placed by me in the hands of the Secretary of Commerce. Attention was forcibly drawn to the serious risks invoked in so complete a national dependence upon foreign sources for a class of products vitally essential to the very existence of our textile and many allied interests. A summary of the report was at once communicated to the Senate (S. Doc. No. 952, 63d Cong., 3d sess.). It appeared also in Commerce Reports No. 47, for February 26, 1915. The full report, entitled "Dyestuffs for American Textile and Other Interests," Special Agents' Series, No. 96, was published by the Bureau of Foreign and Domestic Commerce on March 20th.

On May 1st I was instructed to study carefully existing conditions in the dyestuff industry. Visits were paid to all companies engaged in the manufacture of coal-tar derivatives, including several newly organized undertakings. An exhaustive report on this subject appeared in Commerce Reports, No. 115, for May 17, 1915. It soon passed into a second edition in the form of a separate reprint.

In the concluding paragraphs of this report it was shown that the available stock of dyes of German origin would probably be exhausted before the close

*From an address delivered Dec. 20, 1915, before the Cincinnati Section of the American Chemical Society.
†U. S. Bureau of Foreign and Domestic Commerce.

of the summer. Strong emphasis was laid upon the imperative necessity of making timely provision for such a blow on the country's textile and allied industries. The prompt use on an extended scale of natural and mineral dyes was urged, and the pressing need of economy in the employment of coloring materials was fully demonstrated.

As a matter of fact, the warning was heeded. Every possible device was called into play to reduce the quantity of dyestuffs used. The average textile mill husbanded its stock of colors so as to make it reach until about October 1st. Since then the shortage has been increasingly felt. One mill after another has been forced to close entirely or in part.

A single instance is typical. The largest full-fashioned hosiery mill in the United States (and in the world) employs 2,500 operatives. Ordinarily it requires 500 pounds of dyestuffs daily to cover the needs of its dyehouses. On October 1st its stock of colors had sunk to half a barrel. Some 160,000 dozen pairs of hose were stacked up awaiting dyes. Over 1,000 operatives were enjoying an unwelcome vacation. With considerable difficulty the manager has secured a ton of aniline oil, to use for aniline black, at a cost per pound of \$1.50. (The price in July, 1914, was 10 cents.)

The files of my correspondence show that similar conditions exist in all the branches of industry depending upon the factor of color. In every sense of the word, American textile and allied interests are facing an acute "dyestuff famine." The occasional arrival of small lots of Swiss colors, or of other artificial colors, secured by various means in out-of-the-way corners of the world, serves only to accentuate the seriousness of the situation. South America and the Far East have been searched for this purpose with exceptional diligence.

The question naturally arises in every quarter, what has the Government done to alleviate the hardships of such a famine, and what is it now doing?

The reply may be briefly formulated. Two departments of the Government only come into consideration in this connection.

The Department of State, for eight months, has exerted every possible effort to secure the free passage of German dyestuffs to our ports. Although, thus far, no results have been obtained, it continues its efforts without relaxation.

The Department of Commerce published in March, 1915, its exhaustive study of the dyestuff situation in the United States, outlining all the factors in the case. In May, it warned all industries concerned of the impending dangers. Since last February it has done all in its power to inform consumers of colors how they can most easily lessen the hardships incident to a shortage in dyes. It has inculcated economy in the use of dyestuffs generally. It has pointed out the desirability of employing natural coloring materials on the most generous scale. It has encouraged and stimulated every

undertaking promising to add even the smallest amount to the available supply of dyes. It has done all in its power to prevail upon capital and enterprise to enter the field of coal-tar chemistry, to increase the supply of coal-tar "crudes," to multiply the production of intermediates, to broaden and intensify the output of American-made, finished dyestuffs. It has brought together inventors and capitalists, the producer of colors and the consumer of colors.

It has recognized the fact that all industries dependent upon the factor of color must suffer more or less from the existing conditions, and has urged a mutual spirit of conciliation and compromise between the consumers of colored fabrics and articles and the manufacturers of these wares.

With each added month of the current year it has become increasingly evident that American capital and American enterprise are ready to join in creating a national dyestuff industry, should it be assured of adequate protection against unfair competition on the part of foreign rivals when normal international exchanges are re-established. The needs of the case were carefully studied by the Federal Trade Commission and by the Department of Commerce.

On September 30th, in a communication from the Secretary of Commerce to the Chief of the Bureau of Foreign and Domestic Commerce, the attitude of the Department in this connection was briefly but clearly formulated.

On October 22nd, in an address before the New York Section of the Society of Chemical Industry, the chief of this bureau defined more fully the attitude of the department, in its conviction that adequate legislation was urgently needed to protect those embarking in a comprehensive coal-tar dyestuff industry against the danger of "dumping" and determined underselling on the part of the foreign competitors, hitherto dominating this branch.

Since then, it has been officially announced that such legislation will be earnestly requested from Congress at the present session.

It is now confidently hoped that American enterprise in the field of synthetic colors will soon be amply protected by a statute making as impossible in foreign trade, as it is in domestic trade, any attempt to crush, stifle, and throttle a new industry on the part of competing rivals beyond the seas.

It remains now to outline what has actually been accomplished toward a material alleviation of the hardships of this period of famine through which we are passing, and to what extent the foundations are being laid for an independent American coal-tar chemical industry.

The present dyestuff famine has made unusual demands upon the adaptability and ingenuity of the American people. It has involved readjustments all along the line, throughout the entire sequence of links connecting the cotton fields of our southern states, the flocks of sheep in distant Australia, the feeders of silk-

worms in the Far East, with the gayly appareled throngs on our streets. The problem is being attacked from three different angles.

In the first place, the few existing American establishments devoted to the manufacture of artificial dyestuffs have notably increased their production. Prior to the war they made a somewhat limited amount of coal-tar colors. The annual output was about 3,300 short tons. For the purpose of their manufacture, intermediates were imported, chiefly from Germany. These were assembled into finished dyes by the aid of a few American chemicals, and by the labor of not over 400 workmen.

With a nearly total cessation in the importation of intermediates came the necessity for a complete revolution in the organization of the modest American industry. Prompt and resolute decisions were made. Great sums of money were invested in new plants. Before the war was 12 months old the output of American coal-tar colors had doubled. Too much praise cannot be given to the men who accomplished this *tour de force*.

This involved a notable increase in the production of coal-tar crudes. It also called into existence a number of new companies engaged in the manufacture of intermediates, especially of aniline.

The domestic supply of the crudes has now assumed large proportions. The approximate monthly output at present, in short tons, is: Benzol, 7,500; toluol, 1,870; xylol, 950; naphthalene, 12,500; phenol, or carbolic acid (largely synthetic), 10,000 tons. Unfortunately, the demand for phenol, benzol, and toluol, to be used in the manufacture of explosives, is now so abnormally high that there has been some difficulty in securing enough for the makers of coal-tar intermediates. The manufacture of these latter, especially of aniline, has suddenly grown to considerable proportions and is constantly increasing. There are over 17 firms engaged in this branch and others are entering the field. There are 14 firms now engaged in making finished coal-tar dyestuffs.

A list of the firms now occupied with the manufacture of coal-tar derivatives is here given, in view of the multitude of inquiries regarding American sources of the coal-tar products, formerly secured from European manufacturers:

MANUFACTURERS OF COAL-TAR CRUDES.

The Barrett Manufacturing Co., 17 Battery place, New York City.

Bayway Chemical Co., Bayway, Elizabeth, N. J.

Baird & McGuire (Inc.), 23 Allerton street, Roxbury, Boston, Mass.

Sammel Cabot (Inc.), 141 Milk street, Boston, Mass.

Isaac Winkler & Bro., Cincinnati, Ohio.

Thomas A. Edison, Inc., Orange, N. J. (synthetic carbolic acid; monthly 150 short tons).

American Coal Refining Co., Denver, Colo.

A list of the 74 retort coke-oven plants in the United States on Jan. 1, 1915, is given on page 411 of the

recently issued bulletin on "The Manufacture of Coke in 1914," published by the United States Geological Survey, and forming a part of the report by the Survey on the "Mineral Resources of the United States, 1914." Copies can be obtained by application to the office of the United States Geological Survey, Washington, or to the Superintendent of Documents, Government Printing Office. Practically all of these coke-oven plants are now equipped with benzol-recovery plants and are regular sources of benzol, toluol, and naphthalene.

MANUFACTURERS OF COAL-TAR INTERMEDIATES.

The Benzol Products Co., 25 Broad street, New York City (aniline, substituted anilines and hydroquinone). The extensive works at Marcus Hook, Pa., have received notable additions. It is now the leading source of supply. This company, organized in 1910, was the first to manufacture aniline on a large scale in this country.

Thomas A. Edison, Inc., Orange, N. J. (aniline, paraphenylene-diamine). The monthly production of aniline is 138,000 pounds; of nitrobenzol, 45,000 pounds.

The Midvale Chemical Co., Elizabeth, N. J. (aniline).

The American Synthetic Color Co., Stamford, Conn. (aniline).

The Blackstone Chemical Works, 531 Grosvenor Building, Providence, R. I. (aniline).

Paul Weiler, 326 Front street, Perth Amboy, N. J.

Middlesex Aniline Co., Lincoln, N. J. (aniline).

May Chemical Co., Perth Amboy, N. J. (aniline).

Upton Brothers, Bristol, Ind. (aniline).

The United States Coal-Tar Products Co., 40 West Thirty-second street, New York City (aniline).

Seydel Manufacturing Co., 86 Forrest street, Jersey City, N. J. (aniline).

The Chemical Co. of America (Inc.), Springfield, N. J.; office, 320 Broadway, New York City (aniline).

The Butterworth-Judson Co., Newark, N. J. (aniline).

American Synthetic Dyes (Inc.), Newark, N. J.; office, 60 Wall street, New York City (aniline).

The Monsanto Chemical Works, St. Louis, Mo. (dinitrochlorbenzol).

The Middlesex Chemical Co., Chester, Conn.

The Manhattan Commercial Co., New York City (aniline).

All of the manufacturers of aniline are, naturally, able to supply nitrobenzol.

MANUFACTURERS OF ARTIFICIAL DYESTUFFS.

Schoellkopf Aniline & Chemical Works (Inc.), Buffalo, N. Y.; office, 100 William street, New York City. This is the oldest and most important company engaged in this branch. It was organized in 1870. Prior to the war it manufactured over 100 different dyestuffs. Its colors are used very largely not only by the cotton textile mills, but also by silk, woolen and other industries.

W. Beckers Aniline & Chemical Works, 105 Underhill avenue, Brooklyn, N. Y. The works of this company, completed in June, 1915, are very extensive. It manufactures a large variety of dyestuffs and specializes on colors for the woolen industry, more particularly alizarin substitutes. Capital, \$1,000,000.

Heller & Merz, Newark, N. J.; office, 505 Hudson street, New York City. This company specializes on coal-tar colors used for the manufacture of paper, in connection with its extensive production of mineral pigments.

The Central Dyestuff Co., Newark, N. J. A variety of dyestuffs, for use in all branches, are manufactured.

The Consolidated Color & Chemical Co., Newark, N. J.; office, 122 Hudson street, New York City. The production is limited to a small group of standard aniline dyes, used chiefly in textile mills.

The Bayer Co. (Inc.), Rensselaer, N. Y.; office, 117 Hudson street, New York City. This company manufactures some of the colors which are specialties of the Bayer Co., of Leverkusen, Germany.

The Pearsite Co., Clay City, Ky.; office, 346 Broadway, New York City. This company, recently organized with an authorized capital of \$2,000,000, manufactures a group of six colors from the products of the distillation of cannel coal.

The Federal Dyestuff & Chemical Co., Kingsport, Tenn.; office, 30 Pine street, New York City. This company, organized in October, 1915, with an authorized capital of \$15,000,000, plans for the construction of several plants in different sections of the country. The first plant, at Kingsport, Tenn., is largely devoted to the production on a vast scale of sulphur black.

A. Klipstein & Co., West Charleston, W. Va.; office, 644 Greenwich street, New York City. The recently constructed factory of an old and well known importing house is chiefly devoted to the manufacture of sulphur dyes—brown, and, especially, sulphur black.

The Dow Chemical Co., Midland, Mich. This company has embarked upon the manufacture of synthetic indigo.

The Stanley Anilin Chemical Works, Lock Haven, Pa.; office, 848 Drexel Building, Philadelphia, Pa. This company is devoting its attention largely at the outset to the manufacture of direct blacks for cottons.

The United Securities Dye and Chemical Co., Wilmington, Del. Incorporated December 11, 1915. Authorized capital, \$5,000,000.

Standard Aniline Products (Inc.), Wappingers Falls, N. Y.; office, 366 Fifth avenue, New York City (beta-naphthol, paranitramiline, sulphur black).

The Erik H. Green Co., North Attleboro, Mass.; office, Grosvenor Building, Providence, R. I. (sulphur black).

ANILINE AND ANILINE BLACK.

Aniline itself, when destined for use in dyeing aniline black, should be classed as a finished dyestuff. A

large share of the aniline now being produced is used for this purpose, especially in hosiery mills. When noting that a single firm, such as the Edison Company, is turning out 69 tons of aniline each month, it is possible to grasp what is being done to lay the foundations for a comprehensive American dyestuff industry.

Verbally, and in print, it has seemed necessary to emphasize the eminent desirability of increasing the output of aniline rather than to branch out into the manufacture of a varied list of dyes. Ambitious young chemists are keenly desirous of bringing out at once finished dyestuffs in a greater or less variety. As a rule, they now recognize that they can best serve the textile and other industries dependent upon colors by concentrating their efforts on aniline. The logic of the situation plainly shows that in no other way can they, for the time being, make plant, time, and effort count as effectively in lessening the hardships of the current famine. Four-fifths of our hosiery are dyed black, and the extent to which black is used for both men's and women's apparel is evident to all.

An interesting feature in the evolution of this aniline industry—in the narrower sense of the term—is the introduction of small plants for making the oil, devised more particularly for installation in textile works, consuming relatively limited amounts for the production of aniline black. An enterprising Rhode Island firm, manufacturing itself considerable quantities of the oil, is now installing in various textile mills standard plants capable of producing daily 100 lbs. or more of aniline. Such a plant, built to produce 100 lbs. daily, costs from \$1,500 to \$2,000. The services of a single operative are needed to carry on the transformation of benzol into aniline, with occasional assistance in the moving of heavy objects. The operations and the application of the requisite tests can be entrusted to a man of ordinary intelligence, without chemical education. The ordinary output is 90 lbs. of aniline for each 100 lbs. of benzol employed. At current rates for this hydrocarbon, it is found possible to make aniline at a net cost of from 30 to 40 cents per pound. This compares favorably with the daily quotations of \$1 to \$1.40 for immediate delivery and of \$0.70 to \$0.85 for early contract delivery. Within the past month two textile mills have contracted for larger plants, capable of furnishing 500 lbs. of aniline daily.

The policy of all the companies engaged in the direct manufacture of finished dyestuffs has been eminently a wise one. They have resolutely contracted the range of dyes which they attempt to put on the market. There has been a corresponding increase in the quantity of actual dyes manufactured in a given period.

It is evident to all that, under existing circumstances, every possible effort is to be directed toward enlarging the volume of the output; and this can be secured only by severely limiting the number of different dyes produced, and by corresponding simplifi-

cation in organization and plant. How easily this can be done, without involving any serious hardships to consumers of dyestuffs, can be illustrated from the practice in the silk branch.

Ordinarily silk dyers in the vicinity of New York are accustomed to use a very large variety of colors. Recently one of the leading dyers was requested by me to make out a list of what dyes were absolutely necessary. For purposes of comparison he added also the quantities of each color required annually in his large establishment, in which 3,000 dyers are employed. The following is the list:

Yellow.	Lbs.	Purple	Lbs.
Auramine	1,200	Hofman's Violet N...	600
Azo Yellow	14,000	Methyl Violet 5B...	1,000
Quinoline Yellow ..	1,200	Fast Acid Violet 10B.	5,000
Chrysoidine	3,600	Gray and Black.	
Chrysophenin	1,000	Induline	2,500
Orange IV	3,000	Developed Black:	
		Diazo Black BHN }	10,000
		Diazo Brilliant }	
Green.		Black B.	
Brilliant Green	1,000	Sulphur Black	15,000
Diamine Green G (Direct Green)	1,000	Various Direct Blacks	1,000
		Blue.	
Red.		Alkali Blue 2B.....	4,000
Alizarin Granat or		Charge Blue OB	
Claret	1,500	(Opal Blue)	2,500
Rocellin (Fast Red) ..	7,000	Methylene Blue	10,000
Rhodamine B	2,000	Patent Blue	1,000
Alizarin Red SX.....	2,500	Victoria Blue	12,000
		Sky Blue	1,000

He added that the following colors were very helpful:

Yellow.	Lbs.	Green.	Lbs.
Chrysamine G (Direct Yellow)	1,000	Malachite Green	1,000
Blue.		Wool Green S.....	1,500
Pure Blue	1,000	Purple.	
Red.		Brilliant iViolet 6B...	1,000
Fraise	1,200	Various Alizarin, Algol, Ciba,	
Direct Red	1,000	Helindon, and Indanthrene	
		Colors.	

As is seen, the actual needs of a leading silk dyer narrow down to 25 different colors. With an adequate supply of these 25 dyes, he claimed that his business would suffer no material hardship. Similar statements regarding the variety of dyes needed would hold good in cotton and woolen branches.

It is a welcome fact in this connection that four well-equipped works are now about to manufacture sulphur black on a large scale, as shown in the list above. Two other works engaged in the production of intermediates have perfected their arrangements to make ample supplies of the dinitrochlorbenzol required in this special branch.

The most interesting feature to note in this development is the establishment recently on our soil of the commercial production of synthetic indigo. This manufacture has been taken up by one of the older chemical companies and with success. The daily output will soon reach 5,000 lbs. of 20 per cent paste. Naturally that can be made is sold for months ahead. Three other powerful firms are carefully studying the possibilities of manufacturing this most important dyestuff.

When one reflects that the great "Badische" company on the Rhine expended \$5,000,000 on its indigo plant and on the necessary research, before a single

pound was placed upon the market, and when we further consider that indigo is upon the free list, the pluck and enterprise now manifested in this field cannot but excite admiration.

While the output of artificial dyes of domestic origin was thus increasing at a rapid rate, it was necessarily far removed from meeting the bulk of the country's demand under normal conditions. Here, the existing equipment in half a dozen large American works, organized for the production on a large scale of natural dyes, has proved to be a national asset of pronounced value.

The methods for using natural dyestuffs, such as logwood, fustic, cutch, etc., have been notably perfected of late. In nearly all branches of textile manufacture it has been found practicable to introduce their use. The current output of dyewood extracts is now about three times as great as it was before the war, and it is constantly increasing. Logwood blue is now in widespread use, instead of indigo, for dyeing denims and similar cotton fabrics.

The silk industry is already accustomed to the use of large amounts of logwood. Dyers of silk fabrics are now attentively studying the availability of other dyewood extracts under existing circumstances. A welcome addition to the domestic supply of natural dyestuffs is the handsome yellow, obtained from the Osage orange of the Mississippi Valley. The dye is the same as that present in fustic. It is, however, a pure compound, free from the varying admixture of a reddish coloring matter, which renders the use of tropical fustic somewhat uncertain. The Forest Products Laboratory, at Madison, Wis., maintained by the Forestry Service of the Department of Agriculture, furnishes full information regarding the application of this new dyestuff and the sources from which it can be obtained. It was in this laboratory that the value of the new color was first demonstrated.

Even with the aid of a vastly increased employment of natural dyestuffs, we meet little over one-half of our customary requirements of organic colors. It has become evident that a serious dislocation in the whole organized system of retailing and using such textile fabrics as involve the factor of color, can be avoided only by a genuine spirit of sympathy and co-operation between the two final links in the chain joining the producers of raw material and the consumers of finished products.

Manufacturers, for example, are practicing a most rigid economy in the use of color compounds. This is exemplified in the use of pencil lines for heavy stripes, in the substitution of outline designs for conventional patterns requiring extravagant quantities of colors, and in analogous directions. There is also a decided tendency to urge the wearing of white articles of apparel.

In order, however, to limit to the utmost the hardships incident to such a pronounced shortage of dyes, the conditions must be met in a brave and common-

sense manner. Unless the American public is willing to see our textile interests thrown completely out of gear, there must be a most pronounced spirit of compromise and adaptation on the part of the ultimate consumer. Whims, fancies, fads, habitudes of the past, rivalries of the future, all must disappear before actual conditions.

Consumers must recognize and accept these existing conditions in a considerate manner, adjusting themselves to limitations in variety of shade as well as in fastness. This will take a vast burden of anxiety from the shoulders of tailors, milliners, and dressmakers. They, in turn, can make more easily their contracts with the retailer. He can deal with greater certainty and assurance with the jobber. The relations of the latter with the manufacturer will be vastly simplified, and he can with increased confidence order supplies to be handled six months or a year hence. It is a long chain. A spirit of generous compromise on the part of the ultimate consumer will give to it the needed strength. A finical, critical, fault-finding attitude will, on the contrary, cause the chain to snap and break.

What is being done to lay the foundations of a genuine, comprehensive, self-contained, American coal-tar chemical industry, one which will free the country ere long from all economic dependence on foreign sources for the element of color, as needed by our vast textile and allied interests?

In reply it may be stated that amid all the great haste to meet pressing and insistent demands, with the enlargement of existing plants and the erection of new plants there is every evidence of thrift and economy. This augurs well for a complete absence of unnecessary overhead charges, as the scope of the industry broadens.

As a rule, the firms now engaged in the production of intermediates contemplate the manufacture later on of finished dyes. Mr. Edison, who has done such magnificent work in this field by his rapid organization of the production on an extensive scale of synthetic carbolic acid and of aniline, does not intend to continue the output of the latter after the close of the current war. With this exception, all of the numerous firms now occupied with the manufacture of coal-tar compounds are planning to continue their production along the lines already taken up, and to enlarge such production or enter upon the manufacture of additional intermediates or finished dyes, as circumstances dictate.

The extent to which capital has been enlisted in the development of the dyestuff industry is indicated in the list of companies now in full operation. Several other smaller companies, lately incorporated for active work in this field, reveal a widespread tendency among investors to enter vigorously upon a campaign to build up a coal-tar chemical industry.

There is quite noticeable an evident effort on the part of some ardent chemists to further the movement by attempting the introduction of hitherto un-

known organic dyes, produced apparently by relatively simple chemical reactions, some from coal products, others from petroleum waste. Such attempts are regarded with a benevolent eye, as are all other efforts made intelligently and earnestly to limit the strain of the dyestuff shortage. Time must elapse before careful and exhaustive testing shows the permanent value of these new dyes, as regards cost of production and actual tinctorial properties.

Possibly some of the new colors, of entirely unknown composition, may possess enough tinctorial value to warrant their use during the period of a distinct color famine. No prophecies can be made as to the permanent value, when brought, under normal conditions, into keen competition with highly perfected coal-tar dyes of standard qualities.

It is distinctly to be regretted that in the daily press statements have occasionally appeared tending to convey the impression that these attempts to produce new dyes—for they cannot be regarded as more than attempts—were destined to revolutionize the whole color industry and immediately solve the problem of a dyestuff shortage. The entire lack of basis for any such optimistic claims I have promptly and repeatedly shown in printed statements and in public utterances. While no intelligent chemist was misled by press announcements of this character, they unfortunately did cause more than one manufacturer, dependent upon the color factor, to feel as if all danger of a "dyestuff famine" would soon be removed.

The conditions favoring the establishment of a permanent, comprehensive, American coal-tar chemical industry are as follows:

The United States possesses all the needed raw materials in abundance, in such amount that it could meet the demands of the world's dyestuff industry. It offers the largest existing market for the consumption of dyestuffs.

Enterprise, inventive talent, and technical ability are present to an almost unlimited extent.

The time is eminently propitious for the establishment of a national industry. All indications point to the continuance for a year or two of conditions—most deplorable in themselves—which favor a period of construction, free from the disturbing element of foreign competition. Capital is ready to enter the new field in ample amount and is daily being invested.

It demands simply an adequate measure of statutory protection against unfair competition on the part of foreign rivals. This, we now have every reason to hope, will soon be accorded.

It is most refreshing to note the indifference to minor side issues manifested by the men who are determined to build up this new industry. But a few years ago discussion would have centered about the tariff. Today the men who are ready to finance a color industry or to throw into it the best of brain and nerve are asking simply for a fair show—laws to prevent a competitor from hitting below the belt.

This marked readiness of capital to now enlist generously in the new effort, this willingness even to establish upon our soil the manufacture of a coal-tar derivative, such as synthetic indigo, without a cent of tariff protection, do they not tell the whole story?

There is possibly one factor lacking to bring rapidly into existence a comprehensive American coal-tar dyestuff industry: that is, the co-operation of a few men possessing highly developed capacity for organization, combined with a perfect experimental command of the exceedingly complex and intricate field of color chemistry in all its ramifications—men such as created in the past the great works on and near the Rhine, or those now directing them. It might be possible to secure such needed co-operation from the large and well-equipped staffs of the four color works at Basel, in Switzerland.

These highly specialized staffs include scores of men of broad experience in the manufacture of the whole range of coal-tar dyes. Most of them have enjoyed in earlier days the advantages of the "Polytechnic" of Zürich, one of the best equipped institutions in Europe for the training of color chemists. Many have served a more or less extended apprenticeship in the gigantic German chemical works.

It is not difficult to imagine a union of forces in this field—a consolidation of interests between the Swiss companies and the American firms now striving to expand, but forced, as it were, to grope in the dark at times. The transfer of a sufficient corps of Swiss expert color chemists to the United States, at this critical moment, would be of untold value in furthering the rapid evolution of the American industry.

It would be possible, by their aid and direction, to attain, as regards time and money, the maximum of economy, in constructing new plants, in adopting the most practical and effective mechanical devices, in applying the most economical methods, in co-ordinating the diversified features of a complicated branch of manufacture, so as to avoid loss of material and restrict the dependence upon highly skilled and expensive labor. At every step in the organization of a new plant, and in the initial months of its operation, directive co-operation of practical experts would insure the establishment of a self-contained coal-tar color industry on American soil, with a minimum of outlay and a maximum of efficiency in the shortest possible period of time. It would probably enable the industry, in its broader phases, to become so thoroughly rooted in the economic life of the country that, upon the return of normal international exchanges, legitimate competition of foreign rivals could be easily and effectually met.

A striking example of how the dyestuff problem of a great nation can be solved by the co-operation of Swiss intelligence and experience is now seen in Russia. The textile and allied interests of the Russian Empire formerly depended chiefly upon Germany for color materials. The largest dyestuff company of

Germany conducted a branch factory in Russia prior to the war. Dependence upon Germany for semi-manufactured material and for finished dyes was quite as pronounced as in our own country or in Great Britain.

The sudden interruption in current supplies of dyes, consequent upon the outbreak of hostilities, was a heavy blow to Russian textile works. A way out has been found by the organization of a strong company, of which the leading dyestuff house of Basel is a constituent member. This latter furnishes an administrative and technical staff—in other words, the "brains" of the undertaking. Capital is supplied by a group of prominent Russian textile manufacturers who at the same time are the chief consumers of the dyes produced.

The arrangement is eminently practical. As in the recent British organization, the consumers of dyestuffs are the owners and controllers of the undertaking, and a continued market for the output is assured. An abundant source of crude material is furnished by the Russian coke works. The requisite factories have been erected at a considerable distance from the present line of military operations.

What has been done so easily and simply in Russia to meet present emergencies and lay the foundation for a future national dyestuff industry can serve admirably as an object lesson to the United States, ordinarily so much more prompt in recognizing and improving industrial opportunities.

The creation of a comprehensive manufacturing plant by an alliance between Swiss experience, enterprise and skill on one side, and the large financial resources under the control of our great textile interests on the other, is a solution by no means difficult of realization. It would assure capital, management, and market, the three essential factors to success.

A less complex, and perhaps more feasible, method of accomplishing the end in view would be found in establishing a comparatively close organic connection between individual Swiss companies and individual American companies already engaged in the active manufacture of dyestuffs, but limited hitherto to a very narrow range of products.

It is well to note in this connection the relations of the Swiss color industry to both the American and the international markets.

The average annual value of the Swiss exports of artificial colors to the United States during the five years ending June 30, 1914, was \$815,911, as follows: Alizarin and alizarin colors, \$1,777; synthetic indigo, \$48,904; other coal-tar colors, \$765,230; total, \$815,911.

In 1913-14, Switzerland supplied 7 per cent of our imports of indigo and 10.6 per cent of the imports of aniline dyes. The import of alizarin was insignificant. Since the outbreak of the war, and the resultant scarcity of artificial colors, the Swiss import has been of great assistance to American textile interests.

The normal production of the Swiss dyestuff works available for export purposes has an annual value of about \$5,500,000. It is equivalent to nearly one-ninth of the German export and could cover alone nearly 60 per cent of the average annual imports of artificial colors into the United States.

Few realize the role which Switzerland has played in the evolution of the artificial dyestuff industry, despite the entire absence in the land of coal and of raw material for the manufacture of chemicals, with the exception of salt. Immediately prior to the war, Switzerland, on the basis of population, was supplying twice as much as Germany relatively, to the world's market for synthetic colors.

Correspondence is now under way which may lead to a more or less close co-operation between the dyestuff interests of the two Republics.

There are several other phases in the evolution of an American color industry which deserve careful attention at the present time.

The first is connected with the somewhat rapid entrance into this field of a number of separate interests, imperfectly acquainted with the complexity of the problem.

It is well known to every one who has studied the fundamental basis of the past dominance of German color chemistry in the world's markets, that the chief cause of this marvelous control lies in the solidarity of the German industry as a whole. It is so organized that all the correlated parts act in unison. They form practically a unit when, in any land, a serious effort is exerted to secure freedom from dependence upon foreign sources of color.

The question now arises, Is it not eminently desirable that a comprehensive American coal-tar industry, striving to supply nearly all American tinctorial needs, with products made from American raw materials, should possess a higher degree of unity—financial, technical, commercial—than is now the case? Is it not of prime importance that all unnecessary overlapping and duplicating of effort be excluded, at least in the formative stage?

The problem is more easily stated than solved. It is economically important, during the initial period, that the industry should be characterized by that unity and solidarity which contribute so largely to the might and effectiveness of the German rival; and yet it must be free from any tendency toward monopolistic power.

For the moment it suffices to express an aspiration, a hope, for economic conditions which may powerfully aid a young industry in bravely holding its own.

STANDARDIZATION OF DYESTUFFS AND METHODS OF APPLICATION.

A very distinct element of strength to a growing domestic color industry would undoubtedly result, from the establishment of a "Bureau of Standards for Dyestuffs," possibly by the combined action of the great textile organizations of the country. Such a bureau could be modeled after the admirable Division

of Chemistry in the well-organized Bureau of Standards of the Department of Commerce. Its function would be to formulate the physical and chemical criteria of purity for all dyestuffs, exactly as is now done for the drugs listed in our pharmacopoeia. In the laboratories of such a bureau—and they would necessarily be vast—it would be as easy and simple to check and control the tinctorial dyestuffs as is now the case for our medicinals.

Such principles of standardization could likewise be applied to the varied methods of the application of colors on the different fibers and on other wares. A single finely equipped bureau could advantageously replace the multitude of laboratories now maintained by rival dyestuff firms or in textile works. Such an institution could effectively protect a half-grown American industry against attempts to depreciate the quality and value of American-made dyes, and could insure a far greater degree of economy in cost of production than otherwise would be possible.

Every one familiar at all with the employment of colors in dyeing can easily picture to himself the enormous advantages resulting from the impartial and exact classification and standardization of all coloring materials encountered in commerce, or the simplification, economy, and certainty attendant upon their use in connection with the different fibers and fabrics, as well as with leather, feathers, ink varnish, paper, etc.

Instead of hundreds and thousands of isolated, blundering attempts to obtain the best dye for securing certain color results, the desired data could be requested by return mail from a national laboratory. If a dyer wished to know exactly under what conditions, and in what quantities, a given dye should be employed to produce certain tinctorial effects upon a specific fiber, with a minimum expenditure of color, the full directions could be obtained, free of cost, with but little loss of time.

A genuine American coal-tar dyestuff industry this country is bound to have, unless all indications prove false. Our textile and other allied interests resolutely demand that they shall never again be exposed to the disasters accompanying such a dyestuff famine as we now face. Such a powerful national organization as the Association of Hosiery Manufacturers, at a recent session, unanimously resolved that it would willingly bear the burden of increased tariff duties on dyes of foreign origin, if such be necessary, to insure the establishment upon American soil of a domestic, self-contained color industry.

American chemists insist that the one great branch of color chemistry, now wanting in the cycle of our national industries, shall be created in all its ramifications upon our soil; and that American chemical technology shall no longer be so conspicuously lacking in the most brilliant feature of applied science.

Before the advent of this deplorable war we imported annually about 2,500 short tons of aniline oil and aniline salts. In 1916 over 11,000 tons will be

manufactured on American soil, from American coal-tar crudes.

In 1913 our American color works produced 3,300 short tons of coal-tar colors, made chiefly from German intermediates. We imported 25,700 tons of artificial dyes, 22,000 tons coming from Germany.

Today we are making over 15,000 tons of these colors, all from American coal tar. Are the Nation's color chemists too optimistic in confidently looking forward to the year 1917 as a date when the great bulk of artificial dyes consumed in this country will be made in American works, from American raw material, by American labor?

When this Section, in December, 1920, celebrates the completion of the third decade of its existence, I am confident that it will witness, firmly established in our land, a comprehensive, self-contained, American coal-tar chemical industry, furnishing from the by-products of our magnificent array of coke plants, the nation's needs, not only for artificial colors, but also for high explosives, photographic chemicals, synthetic perfumes and synthetic medicinals.

THE DEVELOPMENT IN THE UNITED STATES OF THE MANUFACTURE OF PRODUCTS DERIVED FROM COAL.*

By H. W. JORDAN.

During 1915 we read statements in the press almost daily, which gave the impression that our American chemical industry was wholly unable to manufacture synthetic coal products, and that the only relief in sight was from the wonderful discoveries of a small group of chemical amateurs, who, having patriotically hurled themselves into the situation since the war began, were on the verge of evolving the entire 900 synthetic coal-tar dyes and the whole list of pharmaceuticals from palmetto and other sources, hitherto unsuspected as being fundamental to organic chemical products. These statements, by implication, and by omitting mention of the extensive plants erected and put into operation by the old, established chemical companies in 1915, tended to create the public belief that these companies were doing nothing to supply the American market.

Some of the most important products which were widely heralded as having been produced for the first time in America in 1915, were manufactured by these companies 15 to 30 years ago. Benzol and its homologues have been regular American products, with shipment in carload lots or tank cars, and with occasional exportation to Europe, since 1900. Salicylic acid was manufactured at Jersey City by Zinsser & Company from 1880 until 1897, when foreign competition closed the plant.

Synthetic carbolic acid was manufactured by the Semet-Solvay Company from benzol at Syracuse in

1900 and the following years, in quantities up to 2,500 lbs. daily. This carbolic acid was synthesized into trinitrophenol, commonly known as picric acid, which was bought by the United States Government for use in national defense. The United States had several well-equipped plants, prior to 1885, for manufacturing the principal coal dyes of that day. The industry grew, and produced an increasing number of synthetics, from which all those survive which could surmount the natural and artificial barriers in the road to a complete American coal products industry. The principal ones of these manufacturers have continued without interruption, and constitute the main body of our present organic chemical industry.

The failure to give credit in the daily press for the large amount of capital invested, and for the extensive work accomplished during the past year, is not fair to these American companies which built up our great American chemical industry during the past 30 years, and who are now the prime movers in expanding our American coal products industry to meet the new conditions.

The Benzol Products Company is an example of this growth. Organized in 1910 by men long associated with the acid, alkali and coal products industry, it began the manufacture of aniline and aniline salt at Frankford, Pa., in the aniline plant operated several years before by the late Dr. Jayne. Although the company's output of aniline in 1910 was but a small percentage of the American consumption, the English and German producers immediately dropped the price from 10c or 11c per lb., where they had held it for several years, to 9c or 8c per lb.

Most of the American consumers of aniline refused to buy this American aniline at the fair price of 9c to 10c at which it was offered. Instead they followed their usual custom and sacrificed the American producer by supporting the cut-rate foreign producers.

These American consumers were the very ones who rushed to Washington when the war began, and frantically implored the Department of the Interior to dig up right away, quick, through the Division of Mines, some unfailing source of supply to provide the two thousand or more synthetic coal-tar dyes and pharmaceuticals which had required 45 years of German science and organization to develop. The trip to Washington was easy for them. They had been there repeatedly since 1880, whenever a tariff bill was under consideration, to advocate no tariff on dyes.

The Benzol Products Company received the support of a few of the most far-sighted American consumers, who realized that the permanent establishment of aniline manufacture in the United States was of far greater value than the profit for a few years on their purchase of aniline, at 2c per pound below its former price. With their support the manufacture of American aniline was continued.

Since the war, a new plant was built at Marcus Hook, Pa., and put into operation in August, 1915,

*Paper presented at 8th Annual Meeting of the American Institute of Chemical Engineers, Jan. 12 to 15, 1916.

with ultimate capacity equal to the former United States consumption of aniline. Notwithstanding war conditions, which multiplied the price of its raw materials, benzol, sulphuric acid and nitric acid, the company sold its aniline at a price less than half the prevailing market price of aniline during 1915.

This production of aniline, supplemented by that of a few other plants, has supplied the American market to a fairly comfortable extent.

The Benzol Products Company's aniline has been distributed, by preference, to those consumers who employ directly or indirectly the greatest number of people. The important fact is that in 1916 a supply of aniline equal to the former American consumption will be available at fair prices, and that this supply is not coming from mysterious nor untried sources.

Since 1900 the production of benzol has steadily increased in the United States, so that there was enough benzol at all times for the manufacture of dyes, if the industry had been established by the assistance of the Federal Government and by the sustained support of the American textile manufacturers. Not only were both these lacking, but the textile manufacturers persistently favored the English and German producers in preference to any American manufacturers.

Benzol supply is only one factor, and alone it is not sufficient to justify the very heavy investments required to establish an American coal products industry.

In 1915, several steel companies operating by-product coke ovens, installed benzol recovery plants, so that a heavy production of American benzol is assured. When the war ends the output from these plants will be so abundant that it may become available as motor fuel for automobiles. In this service, one gallon of motor benzol gives 15 per cent greater mileage than does one gallon of gasoline.

Under the abnormal conditions and inflated prices caused by the war, many small plants sprung up and have produced products derived from coal, at a profit. At the end of the war, these plants will fall like autumn leaves. A few will struggle on and consume their war profits in hopeless endeavor to establish permanent business. Only those built on a firm economic basis will survive.

The manufacture of products derived from coal is not an industry by itself. It is founded upon, and is an extension of, the manufacture of mineral acids and alkalies, and was created as a means of making a wider market for those acids—sulphuric, nitric, hydrochloric, acetic, for chlorine and the like, and a market for the alkali products, soda ash and caustic soda. For this reason a permanent coal products chemical industry cannot be created in America except by co-operation with, or extension of, the American acid and alkali manufacturing companies.

In 1915, with prices ten to fifteen times normal, it was possible to manufacture some coal products with

large profit in the United States. With the return to normal conditions, we must conduct our processes with keenest attention to the most scientific methods, because losses of 1 or 2 per cent in the steps of manufacture mean bankruptcy.

Proof that Americans sadly lack this scientific detail was given in 1915 by the many serious accidents, fires and explosions in plants manufacturing these products, the cause of which was faulty engineering design, inexperienced superintendence, untidy plant housekeeping and careless workmen. With unconscious humor, we have done homage to German efficiency by ascribing these accidents to the German diplomatic service.

To illustrate the necessity of attention to detail, take synthetic manufacture of carbolic acid. This process, starting from pure benzol, involves five chemical reactions and from ten to fifteen chemical operations, if all by-products be recovered. If an avoidable loss so small as 1 or 2 per cent be permitted in each of these steps, the final yield of carbolic acid would be so low that the process might be a commercial failure. Yet carbolic acid is one of the most simple products to manufacture.

Many others involve more steps, or steps in which the lack of technical skill produces larger loss. For example, a certain product with a normal price of 30c per pound has a possible maximum yield of 100 units attainable by extreme care in manufacture. With moderate care the yield is 88 per cent, and with only ordinary care the yield drops to 75 per cent. Expressed in dollars and cents the result per ton is:

Possible yield.....	100%, 2,000 lbs. at 30c	\$600 per ton
Usual yield.....	88%, 1,760 lbs. at 30c	528 per ton
Common yield.....	75%, 1,500 lbs. at 30c	450 per ton
Loss at 88% yield.....		72 per ton
Loss at 75% yield.....		150 per ton

Approach to 100 per cent technical efficiency is not the only requisite for commercial success. The intricate processes yield numerous by-products. Some are acids and alkalies which must be recovered and returned for use in the process. Others are salts or coal products which must be refined and sold. For many of these no market exists in the United States.

A network of markets must be created for every one of these by-products, either in the United States, in South America, Asia or Europe, if our American coal products industry is to grow with the world and pay reasonable dividends on the investment.

It is not sufficient that American consumers acquire the habit of buying chemicals "Made in the United States." Our chemical industry, to endure, must cover the world's market; indeed, its ultimate success may depend upon an American merchant marine.

The German system of nationalized industry handles this multitude of by-products with military precision, by fitting each one into the particular technical and commercial chink best suited to it, so that all by-products are marketed at or above cost. This permits the main product to be sold at a profit large enough to sustain the normal growth of the plant and to develop

new products, without adding new capital, and in addition, to pay 10 to 25 per cent dividends.

In complete contrast it has been, and is, the policy of our Federal Government to forbid any such interlocking national co-operation.

The coal products chemical industry is vital to national defense. One source of the extraordinary military strength of Germany is her ability to manufacture ammunition, literally from the air and earth, in unlimited quantity. This ability was created by the chemical industry, which built huge works and trained an industrial army of men with the scientific knowledge and technical skill necessary to transform the nitrogen of the air, and certain ones of the coal products, into ammunition. The fundamental reason for the support which the Imperial Government gave to the coal products industry was that Germany should develop a supply of ammunition adequate for national defense and world conquest.

While developing home resources, the German industry bought benzol, carbohic acid and other crude coal products from England, thus absorbing England's commercial and military strength. Meanwhile we were more backward than England, for we were so quick to grasp the red-hot opportunity presented by German dyes and pharmaceuticals at low prices that we did not even take the trouble to produce enough crude coal products to export.

Ammunition cannot be manufactured in sufficient quantity during the exchange of diplomatic notes prior to war; it must be manufactured and stored long in advance of hostilities. One main national defense is that great coal products chemical plants be established and operated steadily at commercial profit during peace, so that they will be instantly available to produce unlimited ammunition during the war.

In 1915 we built many ammunition plants in the United States, every one on an artificial basis; few of them can make a profit at peace prices. Unless the United States establishes a complete and profitable national coal products industry on a basis to keep abreast with all scientific progress, our program of "National Preparedness" will descend to the plane of comic opera.

Nitric acid from the air is one step in such scientific progress. Our supply of nitric acid comes now from nitrate of soda imported from Chili. After the war, if the importations are not obstructed, we will receive nitrates and nitrogenous products manufactured in Norway and Germany by fixation of atmospheric nitrogen. Part of these products will be for fertilizer, part for explosives.

Exhaustion of the nitrate of soda mines in Chili will ultimately make the United States wholly dependent upon this European supply, unless we manufacture our own nitrates and nitric acid from the air.

The potash situation is a parallel condition. With German potash cut off, we have no potash. Various American sources will be brought into operation, but

several years must elapse before we produce all the potash we consume.

Fixation of atmospheric nitrogen as nitric acid will also require several years, even though the Federal Government give the manufacture its strongest support.

Nitric acid is the effective end of every explosive and is the first chemical reagent used in the manufacture of aniline, and thence of indigo and others of the most important coal products and dyes. Without nitric acid, our entire navy, army and coast defense becomes helpless the instant the stock of ammunition is exhausted.

Our entire investment in national preparedness will be wasted money, if it does not include the manufacture of nitric acid from the air on a scale to render us absolutely independent of foreign nitrates.

A reasonable tariff, if formulated upon rational lines, will be of much value in supporting our coal products manufacture. Such a tariff would divide these products into three classes according to their degree of advancement in manufacture, and would levy duties proportionate to this degree. The classes would be: First, crude products. Second, intermediates. Third, dyes, pharmaceuticals and highly refined products. The duties should be: on crudes 10 per cent *ad valorem*; intermediates 20 per cent *ad valorem*; and dyes 30 per cent *ad valorem*.

If a specific duty be included it should be at the rate of $3\frac{3}{4}$ cents per pound on the intermediate class and $7\frac{1}{2}$ cents per pound upon dyes and pharmaceuticals. There should be no specific duty on crude products.

The free list should include coal tar, coal-tar pitch, creosote oil and mineral acids. Natural indigo and other natural dyes of vegetable or animal origin should be placed with synthetic dyes, in Class 3.

Class 1, crude products, should comprise a small list. It should be described as: All crude products of coal produced through destructive distillation of coal, or otherwise, and not refined by more than one distillation, nor refined by any process other than distillation, nor refined nor produced by synthesis, such products being crude light oils, benzol, toluol, xylol, cumol and naphthalene, crude tar acids containing less than 80 per cent pure tar acids, and all other products from coal not otherwise specially provided for, and not medicinal and not colors or dyes, the duty to be 10 per cent *ad valorem*.

The second, or intermediate class, should include all products manufactured from those of the crude products class, and all so-called intermediates, not colors nor dyes nor pharmaceuticals nor medicinal products, such products being phenol, cresol, aniline, anthracene, etc.—duty 20 per cent *ad valorem* and $3\frac{3}{4}$ cents per pound specific.

The third class should include all colors or dyes derived from coal, including indigo, natural and synthetic, and alizarine—dry or suspended in water—and

dyes obtained from indigo or alizarine, and all products derived from coal, which are used for pharmaceutical or medicinal purposes, or other purposes—duty 30 per cent *ad valorem* and 7½ cents per pound specific.

Natural indigo and all dyes, pharmaceuticals and medicines, and all other products derived from natural sources of vegetable or animal origin, and which are used interchangeably with similar products derived from coal, should be included in Class 3.

There should be an anti-dumping clause to prevent unfair competition instituted for the purpose of destroying American industry. A dumping clause must be drafted with utmost care and its working tactfully handled. If it be too drastic, or if handled without good judgment, it will become worthless, or worse, because foreign countries, in retaliation, will inflict the anti-dumping penalty upon any American manufacturers who may sell their goods in those countries at lower prices than in the United States. We cannot afford to take any chances with American industry now that our export trade in manufactures is becoming better established than ever before in our commercial history.

Compulsory working of patents in theory looks attractive. In practice there has been nothing in the history of the coal products industry which could have been changed or improved by it to the slightest degree. Compulsory working of patents has been tried in England, France and Russia as recently as 1907, and proven a total failure in those countries.

As stated by the German authority, Prof. Otto N. Witt, "the success of a coal-tar dye factory is no longer dependent upon the careful guarding of factory secrets as in the past, but upon a systematically arranged plant and the proper distribution therein of the work to be performed, and above all upon skillful commercial management, both within and without the factory."

Lack of technical common school education is a further disadvantage from which we suffer. Our system of early 19th century education includes no technical or trade schools, by which in Germany, the entire population is perfected in 20th century methods for earning their living in 20th century industries. In consequence American labor does not give effective attention to its job, and it is extremely difficult to secure labor in the United States which will give competent attention to the delicate chemical manufacturing operations of the coal products industry.

The essentials for creation in the United States of a complete industry in the manufacture of products derived from coal are: co-operation of the American acid and alkali manufacturers with the coal products industry; co-operation of the American consumers with American producers through long-term contracts to assure us the American market; establishment of the industry on a peace scale big enough to make it a fundamental factor in national defense; establishment

on a profitable commercial basis of the manufacture of nitric acid, by fixation of atmospheric nitrogen; nationalization, or rather internationalization, of the industry to insure a balanced world market for all by-products; development of a system of 20th century common school and technical school education; finally, maintenance of a rational tariff.

That a larger coal products industry will be established in the United States is certain. The degree to which it attains perfection will be in proportion to the extent with which these requirements for its profitable operation are provided.

THERMOMETERS IN DISTILLATION FLASKS.

The Bureau of Standards of the Department of Commerce has just issued Technologic Paper No. 49, entitled "The Emergent Stem Correction for Thermometers in Oil Distillation Flasks."

Complex mixtures of hydrocarbons of different chemical composition are separated into simpler fractions by fractional distillations carried out between definite temperature limits. Such distillations are carried out in laboratory tests in several different forms of flasks, in which the temperature limits fixed by the specifications are measured by mercurial thermometers, the stems of which project out of the flask into the room, and thus cause the thermometers to read too low—i. e., lower than they would read if the bulb and stem were all at the temperature of the oil vapor around the bulb. To find the true temperature of the vapor it is therefore necessary to apply a so-called stem correction to the observed reading of the thermometer. In the paper above referred to these stem corrections have been determined for several different forms of distillation flasks, and it is shown that in oil distillations tests carried out in the interval 200° to 300° C. it may amount to over 15° C. (27° F.), and it is shown that different chemists fractionating the same oil will find quite different results if one applies the stem correction and another neglects to do so.

The paper also gives a very simple method by which the chemist can determine the total correction that he must apply to the observed reading of his thermometer to find the true temperature of the vapor in the flask—i. e., the total correction due to scale error and to emergent stem. The method consists in reading the thermometer when naphthalene is boiled in the flask, and again when anthracene is boiled in the flask. The boiling point of the former has been found to be 218° C. and of the latter 340° C. The amount by which the observed thermometer readings differ from these two temperatures gives the total correction to the thermometer at two points on its scale, and corrections at intermediate points can be found by interpolation.

Copies of this paper may be obtained without charge upon application to the Bureau of Standards, Washington, D. C.



APPLICATION OF PAPER PULP FILTER TO QUANTITATIVE ESTIMATION OF CALCIUM AND MAGNESIUM.*

By S. L. JODIDI, PH. D.,† and E. H. KELLOGG, B. S.‡

INTRODUCTION.

The elements calcium and magnesium play a great role not only in the mineral kingdom, but also in the organic world, since they are absolutely indispensable to both the vegetable and animal cell. The importance of calcium ions for the life phenomena of the cells is easily comprehended when we consider that calcium is contained in bones, muscles, brain, blood, and the glands of animals, as well as in the membrane of plants; that calcium facilitates the transportation of carbohydrates in plants and precipitates the toxic oxalic acid in cells, and so forth.

The magnesium salts, too, display a variety of functions which have been studied, especially in their relation to the functions of calcium. Ever since Ringer¹ has shown that the toxic effect of potassium can be paralyzed by means of calcium, the question of the antagonism between calcium and magnesium, as well as between various salts generally speaking, is being studied and discussed by a number of investigators. Osterhout,² *c. g.*, has demonstrated that the toxic action of pure sodium chloride solution on algae can be inhibited by the addition of calcium chloride.

True and Bartlett³ have shown that calcium salts are absorbed by plants (*Lupinus albus*) at a greater range of concentrations than magnesium salts, and that the calcium salts apparently enable the plants to retain possession of the salts already present, and, further, that there is a certain ratio of magnesium to calcium which favors maximum absorption, while Loew⁴ has demonstrated that the toxic action of magnesium salts on plants can completely be paralyzed by calcium salts. The antagonism which has been shown to exist between calcium and magnesium (and other electrolytes) in plants holds also true for the animal organism as was experimentally demonstrated by Meltzer and Auer,⁵ Loeb,⁶ and others. Inasmuch as in experiments of the above indicated nature the experi-

menter is frequently confronted with the necessity of estimating calcium and magnesium in whole series of culture solutions before and after the plants have grown in them for a certain length of time, or in various plant and animal materials, or in feeding stuffs offered animals as well as in their organs and tissues, a speedy and at the same time accurate method for the determination of calcium and magnesium seems to be indispensable. While the present methods for their quantitative determinations are accurate, they have the disadvantage of requiring too much time. In this paper it will be shown that the pulp filter, which was shown by the writers⁷ to be superior to either filter paper or asbestos for the filtration of the ammonium phosphomolybdate precipitate, can successfully be applied to the filtration of calcium oxalate and magnesium ammonium phosphate as well.

EXPERIMENTAL.

PREPARATION OF CHESTNUT BARK FOR ANALYSIS.

Having occasion to determine calcium and magnesium in a number of chestnut-bark samples, healthy and infected, we have decided to apply the pulp filter to the estimation of these elements. Bark removed from various chestnut trees was cut to small slices, dried, ground, and finally passed through a 30-mesh sieve. The bark powder obtained was burned in an electric muffle oven where the heat was gradually increased to a dull red heat until the residues represented a uniform gray ash, which was used for analysis.

Two grammes of bark ash were carefully dissolved in dilute hydrochloric acid and evaporated to dryness, the treatment with acid and evaporation being repeated three times. The final dust-dry residue was treated with hydrochloric acid, filtered and thoroughly washed with hot water. Filtrate and washings from the insoluble residue—which consisted of silica, sand, and carbon—were cooled and made up to 500 cc. Of this solution (*S*) several portion of 50 cc. each were treated as follows: On being neutralized with ammonia, the solution was slightly acidified with acetic acid, when 0.5 cc. of ferric chloride and 5 to 6 cc. of concentrated ammonium acetate solution were added and the whole heated to boiling. The brown precipitate (basic ferric, aluminic—phosphate and acetate) was rapidly filtered off and washed with a boiling hot very dilute solution of ammonium acetate, filtrate and washings being used for calcium estimation.

GRAVIMETRIC ESTIMATION OF CALCIUM.

The ordinary⁸ method of calcium determination in-

*From the Journal of the Franklin Institute. Amplified form of a paper presented before the Second Pan-American Scientific Congress, Washington, Jan. 4, 1916, and published by permission of the Secretary of Agriculture.

†Office of Plant Physiological and Fermentation Investigations, Bureau of Plant Industry, U. S. Department of Agriculture.

‡Journ. of Physiol., 3, 389 (1880-82); 4, 29 (1883-84); 5, 247 (1884-1885).

¹Journ. Biol. Chem., 1, 366 (1905-06).

²True, R. H., and Bartlett, H. H., U. S. Dept. of Agric., Bureau of Plant Industry, Bull. 231, 1912; Amer. Journ. Bot., 2, 255 (1915); 2, 311 (1915). See also True, Rodney H., Amer. Journ. Bot., 1, 255 (1914).

³Landwirtsch. Jahrb., 46, 733 (1914); Biochem. Zeitschr., 38, 236 (1912).

⁴Centralbl. f. Physiol., 21, 788 (1907); Biochem. Zeitschr., 38, 238 (1912).

⁵Biochem. Zeitschr., 32, 308 (1911).

⁷Jodidi and Kellogg, Biochem. Bulletin, vol. 4, 1915.

⁸Fresenius, "Quantitative Chemical Analysis," vol. 1, pp. 235-236 (1903).

volves, as is known, repeated decantation, filtration, and washing of the calcium oxalate precipitate, which, if magnesium is present (as was the case with the chestnut-bark ash) has to be redissolved and reprecipitated, which necessitates a repetition of all mentioned operations. The final calcium oxalate obtained is on drying to be separated from the filter, in order to be burned separately, etc. The employment of the paper pulp filter, which completely retains the calcium oxalate precipitate despite rapid filtration, permits of doing away with most of the above operations, which require considerable time, labor, and attention. The method adopted for the work with the pulp filter was as follows:

A Gooch crucible is placed in a somewhat larger platinum⁹ crucible with cover and both are heated, cooled, and weighed together. The Gooch crucible is now placed in the funnel of a suction flask, provided with a pulp filter, whereupon the calcium¹⁰ oxalate obtained, as usual, with ammonium oxalate in slightly ammonical solution is (on standing for 12 hours), *together with the supernatant liquid, at once filtered*¹¹ off into the crucible. The beaker, in which traces of calcium oxalate may remain, is now rinsed out several times with boiling hot water, which is also used for washing the precipitate in the Gooch. The operation of filtering off the precipitate and washing it free from foreign matter goes very rapidly, taking altogether above five minutes. Because of the presence of not insignificant proportions of magnesium in the chestnut-bark ash, the precipitate in the Gooch crucible is now redissolved by means of hot dilute hydrochloric acid—which can be added by stirring up the precipitate with a stream from the nozzle of a wash bottle—and thoroughly washed with hot water. Solution and washings are allowed to run into the precipitation beaker, where the redissolved calcium oxalate is heated to boiling and, with addition of a few cubic centimeters of ammonium oxalate and of ammonia in some excess, reprecipitated. On standing on the steam bath for about 30 minutes the precipitate, on being stirred up with the supernatant liquid, is filtered off quantitatively on the same pulp filter and thoroughly washed with hot water. The Gooch is now placed in the platinum crucible (with which it was weighed) and the precipitate with the pulp filter is directly¹² heated over the Bunsen burner, the small flame of which is at first cautiously directed towards the fore-part of the inclined crucible, where there is no substance, in order to remove the moisture. When the flame is gradually increased and moved backwards it causes the pulp filter first to carbonize, and, when it begins to burn, it is very readily burned to ash, sometimes with sparking, throughout the whole mass,

due to the more or less finely divided state of the paper fiber of which the pulp filter is made up. By finally burning the substance in the covered crucible over the blast¹³ burner, as usual, it is finally converted to calcium oxide. The results are presented in Table I.

TABLE I.

Chesnut-bark Ash, alysis.	No.	No.	CaO found.		Remarks.
			Gramme.	Pct.	
1	*	* 1 ¹⁴	0.0947	47.35	This was healthy bark taken from a chestnut tree about 14 years old, with a periphery of 15½ inches. Only the top of the chestnut was still living.
		* 2	0.0947	47.35	
		3	0.0949	47.45	
2	*	* 4	0.0840	42.00	The infected bark of No. 2 was taken from the same chestnut (see No. 1). The canker was one year old.
		5	0.0839	41.95	
3	*	* 6	0.0868	43.40	This was healthy bark taken from a chestnut tree 22 years old. Only the upper branches of the tree were covered with leaves.
		* 7	0.0870	43.50	
		8	0.0876	43.80	
4	*	* 9 ¹⁵	0.0867	43.35	The infected bark of No. 4 was taken from the same tree as in No. 3. The canker was one or two years old.
5	*10	11	0.1005	50.25	No. 5 was made up of barks taken from several infected trees. The cankers were from one to three years old.
			0.1016	50.80	

While the question of any relationship between the fungus metabolism, on the one hand, and the percentage of the inorganic constituents in the barks, on the other, needs considerably more data and will be discussed in another paper, it may be mentioned here that the corresponding healthy and infected chestnut-bark samples were taken from the same trees in order to exclude the influence of age, since the percentage of calcium in bark usually increases with age, just as the proportion of magnesium decreases. A glance at Table I shows that the analyses Nos. 1 and 2, the precipitates of which were filtered through pulp, agree well with each other, just as they agree with the check analysis No. 3, the precipitate of which was filtered through standard quantitative filter paper. This is also true of all the other analyses, despite the fact that the filtration¹⁶ and washing on the pulp filter takes only some 5 minutes, instead of from 30 to 35 minutes required for the paper filter.

Since, in the presence of magnesium, calcium oxalate has to be redissolved and reprecipitated, as was the case with the chestnut-bark ash, it means that the application of the pulp filter to the calcium determination enables one to save in this case about one hour's time for each analysis, which is especially important when series of analyses are to be made.

When in analytical (or synthetical) work the precipitate only is desired, the substance may be filtered through the pulp filter into an ordinary suction flask. If, however, both precipitate and filtrate are neces-

⁹The platinum crucible is used to prevent loss, which could occur if the pulp filter with the calcium oxalate would be heated directly in the Gooch crucible.

¹⁰The precipitation of calcium took place always in 50 c.c. of solution (S), equal to 0.2 gramme of bark ash.

¹¹The filtrate is, as a rule, faultlessly clear, and does not need any refiltration.

¹²The precipitate with the filter may, of course, be warmed in the oven until nearly dry before they are burned; the drying, however, is not necessary for obtaining good results.

¹³Or Meker's burner.

¹⁴In the analyses designated with a * the calcium oxalate precipitate was filtered on a pulp filter, while in the rest of the analyses, which represent the controls, the precipitate was filtered on quantitative filter paper (S. & S. No. 590).

¹⁵The check analysis corresponding to No. 9 was lost.

¹⁶Decantation is here unnecessary.

sary, it is best to catch the filtrate directly in the vessel—beaker, dish, or flask—in which it is intended to subject the filtrate to further treatment, thus doing away with the necessity of transferring the filtrate from the suction flask to the desired vessel, which involves loss of time and labor as well as dilution of the substance. For the purpose indicated, we are employing to our full satisfaction Witt's¹⁷ filtering apparatus. Instead, however, of a ground-in funnel, we are using the Gooch crucible placed in a filter funnel which fits in a one-hole rubber stopper. The stem of the funnel is bent so as to touch the wall of the receiving beaker (or flask), thus avoiding loss of substance through spattering. A crystallizing dish may conveniently be used as support for dishes or small beakers. For catching filtrates in large flasks or dishes we are using the bell-jar filtering apparatus with the arrangement employed in Witt's apparatus.

VOLUMETRIC ESTIMATION OF CALCIUM.

In the determination of calcium by titrating the oxalic acid combined with it with standard potassium permanganate solution, it is recommended in the literature¹⁸ that, prior to the titration, the calcium oxalate precipitate be quantitatively separated from the filter paper. This, of course, requires additional work. Our observations go to show that the pulp filter in no way interferes with the accuracy of the titration. We proceed as follows: The calcium oxalate precipitate, filtered and washed on the pulp filter, as outlined in the gravimetric estimation of calcium, is by means of a glass rod transferred to the precipitation beaker, together with the pulp filter. To remove traces of calcium oxalate from the Gooch crucible, the latter is placed in a glass funnel under which the precipitation beaker stands. Now hot dilute sulphuric acid (some 350 cc. of water + 10 cc. of concentrated H_2SO_4) is poured on the Gooch, whereupon the beaker content is stirred for a few seconds with a glass rod which reduces the pulp filter cake to pulp and dissolves the calcium oxalate completely. On heating to about 70 to 80° C., the oxalic acid is titrated with standard potassium permanganate solution, usually tenth-normal. The volumetric estimation of calcium as outlined can be accomplished in very much less time than by the ordinary method. Thus, five consecutive volumetric calcium estimations to which the pulp filter (prepared from S. & S. paper filters, No. 589) was applied required 1 hour, which means 12¹⁹ minutes per analysis. Yet the analyses in all of which equal volumes of the same calcium chloride solution were employed closely agreed with each other, the figures in question being, respectively, 14.75, 14.73, 14.78, 14.77, 14.70, cc. of $\text{n}/10\text{KMnO}_4$. In order to have an

impartial judgment as to whether or not the pulp filter gives as accurate results as standard quantitative filter paper, it was deemed advisable to run a number of parallel analyses, which are reported in Table II.

Chestnut-bark ash No.	Analysis No.	Standard KMnO_4 used, cc.	TABLE II. CaO Found.			Remarks.
			Gramme.	Per Cent	Average.	
1	* 1	33.25	0.0936	46.80	46.85	Check analysis corresponding to analyses Nos. 1 and 2 was lost. 1 cc. $\text{KMnO}_4 = 0.002814714$ gr. CaO .
	* 2	33.33	0.0938	46.90		
	* 3	29.60	0.0830	41.50		
2	* 1	29.60	0.0830	41.50	41.40	1 cc. $\text{KMnO}_4 = 0.0028045$ gr. CaO .
	* 5	29.39	0.0824	41.20		
	* 6	29.50	0.0827	41.35		
3	* 7	29.70	0.0833	41.65	43.08	1 cc. $\text{KMnO}_4 = 0.0028045$ gr. CaO .
	* 8	30.63	0.0859	42.95		
	* 9	30.80	0.0861	43.20		
4	* 10	30.70	0.0861	43.05	42.72	1 cc. $\text{KMnO}_4 = 0.0028045$ gr. CaO .
	* 11	30.70	0.0861	43.05		
	* 12	30.42	0.0853	42.65		
5	* 13	30.50	0.0855	42.75	49.97	1 cc. $\text{KMnO}_4 = 0.0028045$ gr. CaO .
	* 14	30.50	0.0855	42.75		
	* 15	30.19	0.0847	42.35		
6	* 16	30.42	0.0853	42.65	49.90	1 cc. $\text{KMnO}_4 = 0.0028045$ gr. CaO .
	* 17	30.12	0.0845	42.25		
	* 18	35.68	0.1001	50.05		
7	* 19	35.52	0.0996	49.80	49.97	1 cc. $\text{KMnO}_4 = 0.0028045$ gr. CaO .
	* 20	35.68	0.1001	50.05		
	* 21	35.60	0.0998	49.90		
8	* 22	35.79	0.1004	50.20	49.97	
	* 23	35.50	0.0996	49.80		

An examination of Table II reveals the fact that the analyses whose calcium oxalate precipitates were filtered through pulp show concordant results, agreeing at the same time with the check analyses whose precipitates were filtered on good quantitative filter paper (No. 590, S. & S.). This is true, *e. g.*, of analyses Nos. 3 and 4, on the one hand, and 5, 6, 7, on the other, or of 18, 19, 20, on the one side, and 21, 22, 23, on the other.

The question naturally arises as to whether or not the methods described for estimation of calcium in chestnut-bark ash have general applicability. To answer this question the following experiments were performed.

Twenty grammes of calcium chloride (CaCl_2 , 29g.) were dissolved in water and made up to four litres. In six portions of this solution the calcium was precipitated as oxalate in the ordinary way, with the results recorded in Table III.

TABLE III.			
CaO No. of Of solution found, analysis used, c.c. gramme.			Remarks.
1.....	50	0.0859	The calcium oxalate precipitates were left in the beakers over night and were filtered next morning on S. & S. paper filters, No. 590.
2.....	50	0.0855	
3.....	25	0.0422	
4.....	25	0.0423	
5.....	25	0.0425	
6.....	25	0.0423	
Average in 25 c.c.		0.0425	

¹⁷A new analytical suction filter which does not seem yet to be on the market and is in the main a modification of Witt's filtering apparatus is described in *Journal of the American Chemical Society*, 37, 1519 (June, 1915).

¹⁸Abderhalden, "Handbuch der biochem. Arbeitsmethoden," vol. 1, p. 407 (1910). Hoppe-Seyler's "Handbuch der Physiol. und Pathol. Chem. Analyse," p. 545 (1909). C. Neuberg, "Der Harn," vol. 1, p. 169 (1911). Treadwell, "Analytical Chemistry," First Edition, vol. II, p. 491.

¹⁹From the beginning of the filtration of the calcium oxalate to the end of the titration.

²⁰The * in front of the numbers designates the pulp filter was applied to the analyses in question, while in the rest of the analyses filter paper (S. & S., No. 590) was employed for the filtration of the calcium oxalate precipitate.

In ten other portions of the above solution the calcium precipitated in the form of oxalate was filtered on standing on the steam bath for from 15 to 30 minutes. The results obtained are expressed in Table IV.

TABLE IV.

No. of analysis	Of solution used, c.c.	CaO found, grammes.	Remarks.
1.....	25	0.0422	In Nos. 1, 2, 7, 8, 9, and 10 the
2.....	25	0.0425	calcium oxalate precipitates ob-
3.....	25	0.0427	tained in the ordinary way were
4.....	25	0.0424	allowed to stand on the steam
Average....		0.0424	bath for half an hour prior to
5.....	25	0.0424	their filtration, while in Nos. 3,
6.....	25	0.0424	4, 5, and 6 the precipitates were
7.....	25	0.0421	filtered on standing on the
8.....	25	0.0424	steam bath for but 15 minutes.
9.....	25	0.0426	
10.....	25	0.0423	
Average....		0.0424	

From the data presented in Tables III and IV it is evident that from pure calcium chloride solution the calcium could be precipitated quantitatively within 15 to 30 minutes. Since the analyses Nos. 1 to 4 whose calcium oxalate precipitates were filtered through good filter paper (S. & S. filters, No. 590) closely agree with the analyses 5 to 10 whose precipitates were filtered through paper pulp, it follows that the pulp quantitatively retained the calcium oxalate precipitates despite rapid filtration.

In six further portions of the above calcium chloride solution the calcium oxalates filtered and washed on pulp were titrated with standard potassium permanganate solution as outlined in this paper. The results in question are expressed in the table below.

Examination of Table V reveals the fact that the volumetric analyses show concordant results which stand in good agreement with the corresponding grav-

TABLE V.

No. of analysis	Of solution used, c.c.	Standard F.MnO ₄ used, c.c.	Corresponding CaO, grammes.	Remarks.
1.....	25	15.03	0.0423	1 c.c. KMnO ₄ = 0.002814714 gr. CaO.
2.....	25	15.03	0.0423	
3.....	25	15.01	0.0422	
4.....	25	15.04	0.0423	
5.....	25	15.05	0.0424	
6.....	25	15.04	0.0423	
Average.....			0.0423	

imetric analyses recorded in Table IV. Thus the data obtained with calcium chloride solution fully confirm the results secured with chestnut-bark ash. In other words, the paper pulp is generally applicable to the quantitative estimation of calcium, no matter whether it is to be determined in inorganic compounds or in biological materials.

In all of the calcium estimations reported in this paper (see Tables I to V) the filtrates from calcium oxalate filtered on paper pulp were, as a rule, at once perfectly clear, in spite of the fact that the quantitative filtration and complete washing of each individual calcium oxalate precipitate required but 5 or 6 minutes. In one or two cases, however, the calcium oxalate passed through the pulp filter and refiltrations were necessary. It seemed desirable more definitely to ascertain the conditions under which the calcium

oxalate precipitate passes through the pulp filter, or is completely retained by it. With this object in view 10 grammes of calcium chloride were on solution in water made up to 2 litres. Various portions of this solution were uniformly made up with water to a total volume of 200 cc., heated to boiling when the calcium was precipitated with boiling-hot ammonium oxalate solution, and the whole made slightly ammoniacal. On standing on the water-bath for about an hour, the precipitate was stirred up and together with the liquid filtered on a pulp filter, washed with hot water, and titrated with standard potassium permanganate solution. The results are summarized in Table VI.

TABLE VI.

No. of analysis	Of solution used, c.c.	Filtration required, c.c. minutes.	KMnO ₄ used, (1 c.c. = 0.0028595 gr. CaO).	Corresponding CaO, grammes.	Remarks.
1.....	10	0.7	5.75	0.0164	Filtrate (from calcium oxalate) perfectly clear.
2.....	10	0.6	5.71	0.0163	Filtrate perfectly clear.
3.....	25	0.6	14.90	0.0415	Filtrate perfectly clear.
4.....	25	1.0	14.53	0.0415	Filtrate perfectly clear.
5.....	50	2.0	29.20	0.0835	Filtrate perfectly clear.
6.....	50	2.9	29.20	0.0335	Filtrate perfectly clear.
7.....	100	14.0	58.30	0.1607	Filtrate not quite clear. One refiltration gave clear filtrate.
8.....	100	...	...	...	very cloudy. Refiltration unsuccessful.
9.....	200	...	...	...	Filtrate very cloudy. Three refiltrations did not give clear filtrate.

From the data given in the table it would appear that the concentration of the liquid in which calcium is precipitated as oxalate plays a considerable role. In other words, *ceteris paribus*, the calcium oxalate precipitates formed in dilute solutions seem to consist of better, larger crystals which filter well through pulp and give at once perfectly clear filtrates. Thus the filtration (and washing) of calcium oxalate on a pulp filter requires the less time, the smaller is the amount of calcium used. The filtrate from calcium oxalate was perfectly clear so long as the amount of calcium oxide ranged from about 0.01 gramme CaO (or less) to 0.10 gramme CaO. When amounts larger than 0.10 gramme CaO (= 0.23 gramme calcium oxalate) are analyzed, the filtrate from calcium oxalate is cloudy, provided the precipitation of calcium oxalate takes place in a volume of but 200 cc. of liquid.

From the above it would follow that in analyzing larger amounts of calcium it is necessary to precipitate it as oxalate in larger volumes in order to get at once clear filtrates, which was actually confirmed by experiments. At any rate, in the application of the pulp filter to the analysis of calcium it is, for the reasons stated, advantageous to use small amounts of sub-

stance. In this connection it seems reasonable to assume that the difficulties encountered in the filtration of calcium oxalate precipitates, which not infrequently pass² through paper filters and necessitate repeated refiltration, may in part be due to the fact that the precipitation of calcium as oxalate is performed in not dilute enough solutions.

GRAVIMETRIC ESTIMATION OF MAGNESIUM.

As in the case of calcium, the application of the pulp filter enables one to eliminate tedious operations incidental to the ordinary method of magnesium estimation, such as repeated decantation, filtration, and washing of the magnesium ammonium phosphate precipitate, as well as its drying and separation from the filter before its ashing. The way we proceeded was as follows: The filtrates and washings from the calcium oxalate precipitates (corresponding to 0.2 gramme of chestnut-bark ash) were evaporated on the steam bath to dryness, freed from ammonium salts by gentle ignition, whereupon the residues were treated with dilute hydrochloric acid, filtered and washed quantitatively. In the combined filtrate and washings the magnesium was precipitated, as usual, in the form of $MgNH_4PO_4$, which, on standing for 12 hours, was, *together with the supernatant liquid*, at once filtered and washed with 2½ per cent ammonia on a pulp filter.²¹ The quantitative filtration and washing of the magnesium ammonium phosphate on the pulp filter takes only from 3 to 6 minutes, as against about half-hour required for the paper filter. The Gooch placed in the platinum crucible (with which it was weighed) is now heated directly²² over the burner, at first very cautiously, gradually increasing the flame, and finally igniting the covered crucible over the blast burner until the substance is converted to magnesium pyrophosphate.

TABLE VII.

Chestnut-bark ash analysis	Mg ₂ P ₂ O ₇ found	Corresponding MgO.	
No. No.	Gramme.	Gramme.	Per cent. Average.
1	* 1 ²³	0.0627	0.02272 11.36 } 11.42
	* 2	0.0633	0.02294 11.47 }
	* 3	0.0630	0.02283 11.42 } 11.42
2	* 4	0.0505	0.01833 9.16 } 8.96
	* 5	0.0183	0.01749 8.75 }
	* 6	0.0498	0.01804 9.02 } 9.02
3	* 7	0.0785	0.02845 14.23 } 14.38
	* 8	0.0801	0.02963 14.52 }
	* 9	0.0744	0.02865 14.03 }
4	* 10	0.0781	0.02831 14.16 } 14.12
	* 11	0.0781	0.02831 14.16 }
	* 12	0.0638	0.02311 11.56 }
5	* 13	0.0631	0.02285 11.43 } 11.66
	* 14	0.0652	0.02361 11.81 }
	* 15	0.0653	0.02365 11.82 }
6	* 16	0.0650	0.02354 11.77 } 11.77
	* 17	0.0339	0.01228 6.14 } 6.12
	* 18	0.0337	0.01221 6.11 }
7	* 19	0.0326	0.01159 5.80 } 5.80

*Alderhalden, Handbuch Biochem. Arbeitsmeth., vol. i, p. 406 (1910); Treadwell, Analyt. Chemistry, vol. ii, p. 66 (1907); Fresenius, Quant. Anal., vol. i, p. 235 (1903); Hoppe-Seyler's Handbuch Physiol. and Pathol. Chem. Anal., 8th Edition, p. 545 (1903).

²¹If not otherwise stated, the arrangements for the platinum and Gooch crucibles, for the filtration of the magnesium ammonium phosphate precipitate, and so on, were made exactly as described in the estimation of calcium.

²²Drying the pulp filter with the precipitate prior to ashing is here not essential for obtaining accurate results, as direct experiments have convinced us.

²³As in Tables I and II, the * in front of the numbers designates that the pulp filter was applied to the analyses in question.

In spite of the rapid filtration of the magnesium phosphate precipitate, the results which are expressed in Table VII show that the precipitate is quantitatively retained by the pulp filter, since the magnesium estimations whose precipitates were filtered on pulp agree very well with the check analyses whose precipitates were filtered on standard quantitative filter paper.

It seemed desirable to ascertain the percentage of saving with various kinds of filter paper when used as pulp. Hence, three S. & S. filters, No. 595, of 11 cm. diameter, were reduced with water to pulp which yielded in Gooch crucible twelve pulp filters. Five consecutive volumetric calcium estimations whose calcium oxalate precipitates were filtered through these pulp filters required for the same amount of calcium solution 29.71, 29.70, 29.70, 29.70, 29.72 cc. n/10 $KMnO_4$ respectively. Equally, three S. & S. filters, No. 589, of 12½ cm. diameter, were reduced to pulp which was sufficient for making fourteen pulp filters. Quantitative analyses whose precipitates were filtered through the pulp filters gave accurate results.

In like manner three filters of 9 cm. diameter which were cut from S. & S. sheet filter paper, No. 598, when reduced with water to pulp yielded twelve pulp filters. Three consecutive phosphoric acid estimations, in all of which equal volumes of the same phosphate solution were used, required for neutralization of the yellow precipitates (filtered through the pulp filters) 10.95, 10.81 and 11.00 cc. n/2 NaOH respectively. Two further estimations in which the yellow precipitates were filtered through pulp filters prepared from S. & S. filters, No. 588—which from our previous work were known completely to retain the ammonium phosphomolybdate precipitate—required for neutralization of the yellow precipitates 10.95 and 10.95 cc. n/2 NaOH respectively. Finally, three filters of 11 cm. diameter which were cut from the commonest sheet filter paper (used for technical work) were reduced with 150 cc. water to pulp, to which now 150 cc. of 20 per cent hydrochloric acid were added and the whole left over night. Next morning the pulp mass was sucked off on a "nutsche" and washed with hot water. The washed pulp was shaken with water (450 cc.) to an emulsion which yielded on Gooch crucibles seventeen pulp filters. This experiment was repeated with the same result. Three consecutive phosphoric acid estimations in which the yellow precipitates were filtered through the pulp filters required for neutralization of the yellow precipitates (obtained from equal volumes of the phosphate solution) 11.05, 10.91, 10.90 cc. n/2 NaOH respectively. As check three other estimations were made whose yellow precipitates were filtered through pulp prepared from S. & S. filters, No. 588. They gave respectively 10.80, 10.91, 10.99 cc. n/2 NaOH.

The above analyses show that the pulp filters prepared from various kinds of filter paper quantitatively retain the precipitates in question. For the sake of

convenience the data are expressed in Table VIII.

It is hardly necessary here to mention that the larger and thicker the paper filters are, the more pulp filters they yield on reduction with water, and *vice versa*. The paper filters used in the experiments of Table VIII were of the sizes which are frequently employed in quantitative analysis.

CONCLUSIONS.

1. The application of the pulp filter to the filtration of the calcium oxalate precipitate enables one to eliminate the tedious operations of repeated decantations, filtrations, washings, etc., and to save half an hour for calcium estimation. In case, however, the calcium oxalate precipitate has to be redissolved and reprecipitated, as is, *e. g.*, necessary in the presence of

TABLE VIII.

Kind of paper filters used.	Diameter of paper filters, cm.	Paper filters used, number.	When reduced with water to pulp they yielded (Gooch) number.	Economy of filter paper, per cent.
S. & S., No. 595.....	11	3	12	300
S. & S., No. 589.....	12½	3	14	367
S. & S., No. 598.....	9	3	12	300
Commonest sheet filter paper.	11	3	17	467

a considerable percentage of magnesium, the saving of time is about one hour for each individual analysis.

2. It is possible, by the application of the pulp filter, to make a volumetric calcium estimation in about 12²⁴ minutes, which is about one-third or one-quarter the time necessary for an analysis when filter paper is used for the filtration of the calcium oxalate precipitate.

3. By employing pulp filter for the filtration of the magnesium ammonium phosphate precipitate one is able to do away with the tedious operations incidental to the work with filter paper and to gain about a half-hour's time for each analysis.

4. The work with the pulp filter gives as accurate results for calcium and magnesium as the work with standard filter paper.

5. By using for filtration pulp²⁵ instead of paper, one is able to economize from 300 to 467 per cent of filter paper.

CHINESE INDIGO AVAILABLE.*

The present scarcity of dyestuffs in this country is felt most keenly in the matter of "blacks" and "blues." In fact, were the demands for fast shades of these two colors adequately met, nine-tenths of the burden of anxiety weighing upon the managers of American textile mills would disappear. The arrangements now made upon an exceptionally large scale by the leading American manufacturer of coal-tar dyes to furnish a fast "direct black" will contribute vastly to mitigate

the acuteness of the situation, especially as increased quantities of aniline available for the direct dyeing of aniline black are now made in newly erected works.

The indigo problem becomes, however, more serious each day. Small amounts of synthetic indigo are currently received from Switzerland. Central America contributes a slight quantity of natural indigo, and it is likewise shipped to a very limited extent from Manila, Java, and India. The total receipts from these various sources constitute, however, but a relatively insignificant fraction of the customary supply of indigo ordinarily consumed by our textile and other industries. The "blues" available for cotton by improved methods of applying and fixing logwood are assuming increased importance, especially for denims and allied classes of goods. It takes time, however, to accustom dyers to any such radical alteration in routine methods as that involved in a change from indigo to logwood.

Under these circumstances any additional source of indigo, no matter how limited, possesses importance. The American consulate general at Hongkong reports that stocks of Chinese indigo are now available at that port, and that additional quantities can be secured from interior points in China. It would appear that the production of natural indigo has been notably stimulated of late in Southern China, and that despite the total elimination of Germany's ordinary supply of synthetic indigo to China there is a limited amount of the native product available for exportation. This condition is somewhat surprising in view of the fact that China's normal annual imports of synthetic indigo from Germany are nearly \$7,000,000 in value, and constitute 64 per cent of the latter country's exports of the dye.

The Chinese indigo brought to Hongkong is shipped in cases of about 80 lbs. each. It is in the form of thick paste. The current price per pound at Hongkong is 7.9 cents in gold. Prices at interior points in China are about 15 per cent less.

Samples of Chinese indigo sent to the Bureau of Foreign and Domestic Commerce have been submitted to careful tests regarding the amount of pure indigo (indigotin) present, based upon a comparison of the tinctorial effects produced, with the results obtained from equal amounts of normal 20 per cent synthetic indigo paste. These tests show that the Chinese article contains about 1 per cent of pure indigo.

In order to measure the actual commercial value it must be borne in mind that for every pound of pure indigo present there are 99 pounds of inert matter to be transported. Current commercial samples of the leading grades of natural indigos contain the following percentages of the pure dye:

Java, 68 per cent; Bengal blue, 59 per cent; Bengal Red, 56 per cent; Oude, 44 per cent; Kurpah blue, 55 per cent; Kurpah red, 45 per cent; Madras, 35 per cent; Guatemala, 47 per cent.

²⁵Counting the time from the beginning of the filtration of the calcium oxalate precipitate to the end of the filtration.

²⁶The pulp was obtained from S. & S. filters, No. 589.

*From Daily Commerce Reports.

METALLURGY.

THE CHEMISTRY OF FURNACE EFFICIENCY AND AIR SUPPLY.*

By C. E. LUCKE and E. D. THURSTON, JR.

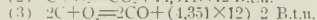
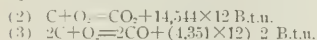
The efficiency of a furnace, or, indeed, of combustion in general, is merely the ratio of the heat actually produced by burning the fuel to the amount originally contained therein. This is equivalent to the heat in the fuel less the combustion losses divided by the heat in the fuel or

$$(1) \text{ Furnace efficiency} = 1 - \frac{\text{loss on combustion.}}{\text{heat originally in fuel.}}$$

These losses occur in the incomplete combustion of carbon to carbon monoxide (CO) instead of to carbon dioxide (CO₂), and in the failure to consume all of the hydrogen and hydrocarbons in the fuel. The latter may be considered as marsh gas (CH₄) as the higher hydrocarbons will break down to form this gas during combustion.

Values for furnace efficiency may be experimentally determined or approximately predicted by empiric equations based on previously determined experimental results. However, by resorting to the chemical equations expressing the reactions occurring during combustion there may be deduced a rational expression for furnace efficiency in terms of the carbon content of the fuel and the composition of the products of combustion as determined from the flue-gas analysis.

Starting with the reaction equations for carbon combining with oxygen to form carbon monoxide and carbon dioxide, Eqs. (2) and (3), and by assuming that the molecular weight in pounds of each of the products formed occupies 358 cu. ft. under standard conditions of pressure and temperature, Eqs. (4) and (5) result:



$$(4) 1 \text{ lb. C} + \left\{ \begin{array}{l} \frac{32}{12} = 2.66 \text{ lb.} \\ \text{or} \\ \frac{358}{12} = 29.8 \text{ cu. ft.} \end{array} \right\} \text{O}_2 = \left\{ \begin{array}{l} \frac{44}{12} = 3.66 \text{ lb.} \\ \text{or} \\ \frac{358}{12} = 29.8 \text{ cu. ft.} \end{array} \right\} \text{CO}_2 + 14,544 \text{ B. t. u.}$$

$$(5) 1 \text{ lb. C} + \left\{ \begin{array}{l} \frac{32}{12} = 1.33 \text{ lb.} \\ \text{or} \\ \frac{358}{12} = 14.9 \text{ cu. ft.} \end{array} \right\} \text{O}_2 = \left\{ \begin{array}{l} \frac{28}{12} = 2.33 \text{ lb.} \\ \text{or} \\ \frac{358}{12} = 29.8 \text{ cu. ft.} \end{array} \right\} \text{CO} + 4,351 \text{ B. t. u.}$$

For air, O₂ = 23.1% and N₂ = 76.9% by weight.
O₂ = 20.9% and N₂ = 79.1% by volume.
N₂ = 3.33 × weight of O₂ and 3.78 × volume of O₂.
Air = 4.73 × weight of O₂ and 4.78 × volume of O₂.

Substituting air for oxygen, Eqs. (4) and (5) become Eqs. (6) and (7) below:

$$(6) 1 \text{ lb. C} + \left\{ \begin{array}{l} 11.517 \text{ lb.} \\ \text{or} \\ 142.44 \text{ cu. ft.} \end{array} \right\} \text{air} = \left\{ \begin{array}{l} 3.67 \text{ lb.} \\ \text{or} \\ 29.8 \text{ cu. ft.} \end{array} \right\} \text{CO}_2 + \left\{ \begin{array}{l} 8.857 \text{ lb.} \\ \text{or} \\ 112.64 \text{ cu. ft.} \end{array} \right\} \text{N}_2 + 14,544 \text{ B. t. u.}$$

$$(7) 1 \text{ lb. C} + \left\{ \begin{array}{l} 5.759 \text{ lb.} \\ \text{or} \\ 71.22 \text{ cu. ft.} \end{array} \right\} \text{air} = \left\{ \begin{array}{l} 2.33 \text{ lb.} \\ \text{or} \\ 29.8 \text{ cu. ft.} \end{array} \right\} \text{CO} + \left\{ \begin{array}{l} 4.429 \text{ lb.} \\ \text{or} \\ 56.32 \text{ cu. ft.} \end{array} \right\} \text{N}_2 + 4,351 \text{ B. t. u.}$$

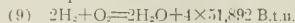
Let X = fraction of a pound of carbon burning to CO₂.

$1-X$ = fraction of a pound of carbon burning to CO.

Multiplying Eq. (6) by X and Eq. (7) by $1-X$, and adding, Eq. (8) results when no excess air is supplied.

$$(8) 1 \text{ lb. C} + 5.759(1+X) \text{ lb. air} = \left\{ \begin{array}{l} 29.8X \text{ cu. ft. CO}_2 \\ + \\ 29.8(1-X) \text{ cu. ft. CO} \\ + \\ 56.32(1+X) \text{ cu. ft. N}_2 \\ + \\ (10,193X + 4,351) \text{ B.t.u.} \end{array} \right.$$

The corresponding equations for hydrogen combustion are given below as Eqs. (9), (10), (11), the lower heating value of hydrogen being chosen. It will be noted that the volume of the water vapor formed is zero, as the vapor will condense to water at the temperature at which the analysis of the products is made, and the volume in the liquid form is infinitely small as compared with that in the vapor condition.



$$(10) 1 \text{ lb. H}_2 + \left\{ \begin{array}{l} \frac{32}{4} = 8 \text{ lb.} \\ \text{or} \\ \frac{358}{4} = 89.5 \text{ cu. ft.} \end{array} \right\} \text{O}_2 = \left\{ \begin{array}{l} \frac{36}{4} = 9 \text{ lb.} \\ \text{or} \\ \text{zero cu. ft.} \end{array} \right\} \text{H}_2\text{O} + 51,892 \text{ B. t. u.}$$

$$(11) 1 \text{ lb. H}_2 + \left\{ \begin{array}{l} 34.64 \text{ lb.} \\ \text{or} \\ 427.8 \text{ cu. ft.} \end{array} \right\} \text{air} = \left\{ \begin{array}{l} 9 \text{ lb.} \\ \text{or} \\ \text{zero cu. ft.} \end{array} \right\} \text{H}_2\text{O} + \left\{ \begin{array}{l} 8 \text{ lb.} \\ \text{or} \\ 338.3 \text{ cu. ft.} \end{array} \right\} \text{N}_2 + 51,892 \text{ B. t. u.}$$

*From School of Mines Quarterly, Columbia University.

All fuels are composed, so far as the combustible goes, of carbon and hydrogen, with possibly a very small and in all cases a negligible amount of sulphur.

Let C^1 = fractional part by weight of the combustible existing as carbon, free or combined;

And $(1-C^1)$ = fractional part by weight of the combustible existing as hydrogen, free or combined.

Multiply Eq. (8) by C^1 , and Eq. (11) by $(1-C^1)$, and add, forming Eq. (12):

$$(12) \left\{ \begin{array}{l} C^1 \text{ lb. C} + (1-C^1) \text{ lb. H}_2 \\ \text{or} \\ 1 \text{ lb. combustible} \end{array} \right\} + \left\{ \begin{array}{l} 5.759 (1+X) C^1 \\ 34.64 (1-C^1) \end{array} \right\} \text{ lb. air}$$

$$= \left\{ \begin{array}{l} 29.8XC^1 \text{ cu. ft. CO}_2 \\ 29.8X(1-C^1) \text{ cu. ft. CO} \\ 56.32(1+X)C^1 + 338.3(1-C^1) \text{ cu. ft. N}_2 \\ (10,193X + 4,351)C^1 + 51,892(1-C^1) \text{ B.t.u.} \end{array} \right.$$

which may be simplified as in Eq. (13):

$$(13) 1 \text{ lb. combustible} + (34.64 - 28.88C^1 + 5.759XC^1) \text{ lb. air}$$

$$= \left\{ \begin{array}{l} 29.8XC^1 \text{ cu. ft. CO}_2 \\ 29.8(1-X)C^1 \text{ cu. ft. CO} \\ 338.3 - 282C^1 + 56.32XC^1 \text{ cu. ft. N}_2 \\ 51,892 - 47,541C^1 + 10,193XC^1 \text{ B.t.u.} \end{array} \right.$$

In the above, the only variables are X and C^1 , the former being obtained from the flue-gas analysis and the latter from the ultimate analysis of the combustible of the fuel. From Eq. (8) it will be seen that the ratio of the volume of CO to the volume of CO_2 in the products is $(1-X) \div X$, or the same as the fractional weight of carbon burning to CO and to CO_2 . Since

$$\frac{\text{CO}}{\text{CO}_2} = \frac{1-X}{X}, \quad X = \frac{\text{CO}_2}{\text{CO}_2 + \text{CO}} \quad \text{and} \quad 1-X = \frac{\text{CO}}{\text{CO}_2 + \text{CO}}$$

When no CO is formed, or combustion of carbon is complete, $X=1$, and the heat produced in Eq. (8) becomes $51,892 - 37,348C^1$; hence

$$\text{Furnace efficiency} = \frac{51,892 - 47,541C^1 + 10,193XC^1}{51,892 - 37,348C^1} \quad (a)$$

$$(14) \quad = 1 - \frac{10,193C^1(1-X)}{51,892 - 37,348C^1} \quad (b)$$

$$= 1 - \frac{10,193C^1 \left(\frac{\text{CO}}{\text{CO}_2 + \text{CO}} \right)}{51,892 - 37,348C^1} \quad (c)$$

Eq. (14) holds true if there be no unburned hydrogen or hydrocarbon, and is in terms of carbon content and flue-gas.

As an example, consider a coal, the combustible of which gave an ultimate analysis of 95% C and 5% H_2 , and for which, on combustion, the flue-gas analysis proved to be CO_2 , 12%; CO, 3.8%; O_2 , 4.7%, and N_2 , 79.5%. From Eq. (14)c,

$$\text{Effic.} = 1 - \frac{10,193 \times 0.95 \times \frac{3.8}{3.8 + 12}}{51,892 - 27,348 \times 0.95} = 86\%$$

Should there also be CH_4 and H_2 in the flue-gas, the heat loss for each must be separately determined

and subtracted from the available heat. This may be done as follows: From Eq. (13) it will be seen that the volume of $\text{CO} + \text{CO}_2$ per pound of combustible is $29.8XC^1 + 29.8(1-X)C^1 = 29.8C^1$ cu. ft.; hence the cubic feet of H_2 or CH_4 per cubic foot of $\text{CO}_2 + \text{CO}$, if multiplied by $29.8C^1$, will give the cubic feet of each per pound of combustible; and if these amounts be multiplied by the heat of combustion per cubic foot of the respective gases, the heat loss to be deducted from the fuel will be found. The heat of combustion of H_2 per cu. ft. is 292 B. t. u., and of CH_4 , 959 B. t. u.

Hence heat loss per pound of combustible due to H_2 is

$$\frac{\text{H}_2}{\text{CO} + \text{CO}_2} \times 29.8C^1 \times 292 = 8,702C^1 \left\{ \frac{\text{H}_2}{\text{CO}_2 + \text{CO}} \right\}$$

and that due to CH_4 is

$$\frac{\text{CH}_4}{\text{CO} + \text{CO}_2} \times 29.8C^1 \times 959 = 28,578C^1 \left\{ \frac{\text{CH}_4}{\text{CO}_2 + \text{CO}} \right\}$$

while that due to CO, as already determined, is

$$10,193C^1 \left\{ \frac{\text{CO}}{\text{CO}_2 + \text{CO}} \right\}$$

The sum of these will give the total loss, and the general equation then for furnace efficiency is Eq. (15), which reduces to Eq. (14) when H_2 and CH_4 are zero.

(15) Furnace efficiency =

$$1 - \left\{ \frac{C^1}{\text{CO}_2 + \text{CO}} \right\} \left\{ \frac{10,193\text{CO} + 8,702\text{H}_2 + 28,578\text{CH}_4}{51,892 - 37,348C^1} \right\}$$

As an example, consider the same coal as before, and a flue-gas analysis of CO_2 , 11%; CO, 3.4%; O_2 , 4.7%; H_2 , 1.1%; CH_4 , 0.3%; N_2 , 77.5%. From Eq. (15), Effic. =

$$1 - \frac{0.95}{0.144} \left\{ \frac{10,193 \times 0.034 + 8,702 \times 0.011 + 28,578 \times 0.003}{51,892 - 37,348 \times 0.95} \right\} = 78.7\%$$

From the flue-gas analysis can also be determined the actual amount of air supplied for combustion. When excess air is used, both oxygen and nitrogen will be added to the in air is constant and equal to 3.78, the amount of oxygen present $\times 3.78$ will give the nitrogen belonging the excess air, and the remainder must have come from the combined air, or that actually utilized for combustion. As the ratio of two amounts of air is the same as that of the respective amounts of nitrogen in each, it follows that

$$(16) \quad \frac{\text{Excess air}}{\text{Combined air}} = \frac{3.78\text{O}_2}{\text{N}_2 - 3.78\text{O}_2}$$

The total air will, of course, be the combined plus the excess.

As an example, consider the flue-gas and coal previously assumed. From Eq. (13) the combined air is

$$34.64 + 28.88 \times 0.95 + 5.759 \times \frac{12}{15.8} \times 0.95 = 11.36 \text{ lb.}$$

$$\text{From Eq. (16), excess} = 11.36 \times \frac{3.78 \times 4.7}{79.5 - 3.78 \times 4.7} = 3.25 \text{ lb.}$$

Total air = $11.36 + 3.25 = 14.61$ lb. per pound of combustible.

SULPHUR ELIMINATION IN COKING PROCESSES.*

By J. R. CAMPBELL.†

Sulphur is known to exist in coal as sulphides and sulphates, as can be determined experimentally. Then there is the so-called organic sulphur, or, sulphur in combination with the carbon, hydrogen and oxygen of the coal, about which much has been written, but nothing definitely proved in an experimental way. In fact, so far as we know, there never has been developed a satisfactory and conclusive method in the laboratory for the direct determination of organic sulphur.

For most coking coals it can be safely assumed that the preponderance of sulphur is in the form of pyrite (FeS_2). When exposed to comparatively low temperatures during the coking process, it loses its sulphur according to the following chemical reaction: $7\text{FeS}_2 = \text{Fe}_7\text{S}_8 + 6\text{S}$. It will be seen, therefore, that six out of the 14 atoms of sulphur (or 42.8 per cent) are expelled, or volatilized. Fe_7S_8 remains in the coke as pyrrhotite, or magnetic sulphide of iron; this accounts for the highly magnetic properties of the powdered coke. A more commonly accepted reaction is $\text{FeS}_2 = \text{FeS} + \text{S}$, in which the straight sulphide of iron is produced with 50 per cent volatilization of sulphur.

In the beehive methods of coke making, air is introduced in sufficient amounts to carry on the distilling and the coking processes, and the sulphur is oxidized along with the other volatile products: First, into sulphur dioxide (SO_2), known by the pungent and suffocating odor emitted from the trunnel head; second, into sulphuric anhydride (SO_3); and, finally, into sulphuric acid, as it comes into contact with the air and moisture. In a properly regulated draft on a beehive oven, there is never complete combustion of the gases. In other words, the coking process should be carried on in a reducing atmosphere and a low-grade producer gas kept issuing from the trunnel head. For coals of about 30 per cent volatile matter, the ratio of air to gas is $3\frac{1}{2}$ to 1. In complete combustion, the ratio is 6 to 1, producing an extremely high temperature in the crown of the oven, 3500°F ., more than enough to cause fusion of the refractories used. A good coking temperature is 2500°C . in the crown of the oven.

It follows then that the sulphur remaining in the coking mass as iron sulphide cannot in any way be affected by the aeration or draft on the oven. Among beehive coke-oven operators there used to be a saying, "the hotter the oven, the more sulphur burned out." In view of the foregoing, this probably never was true unless the aeration was carried to complete combustion of not only the volatile gases but the fixed carbon

itself, in which case the iron sulphide (FeS) would, of course, be oxidized to Fe_2O_3 , and the sulphur liberated as usual. This condition would not be productive of good results, as the percentage of coke yield would be abnormally low and the "ashes," or "braise," correspondingly high. This is evidence that so far as the pyritic sulphur is concerned, any sulphur that is volatile at all is so at comparatively low temperatures through the agencies of distillation, and no practical method of superaeration will help in the least in the further elimination of sulphur.

On the other hand, overheating promotes certain chemical reactions in which sulphur forms compounds with other bodies on which heat has no effect. If the coking process proceeds too quickly, or if the heat is irregular, the desulphurization of the coke is apt to be less complete. In these matters much depends upon the skill and judgment of the burner.

In the by-product oven, which is essentially a true distillation process, the heat being applied externally and no air supplied to the oven itself, the sulphur is distilled from the pyrite as atomic sulphur as previously explained but apparently it afterward combines with the hydrogen of the coal gas, forming sulphuretted hydrogen (H_2S), for it is necessary to remove this very objectionable gas before artificial gas can be used for domestic purposes. This is accomplished by the use of hydrated oxide of iron, a by-product now obtainable from mine-water purification.

Here again appears the fallacy of superaerating beehive ovens to eliminate sulphur, for in by-product ovens in which no air is admitted there is just as much desulphurization of the coke as in beehive process; in fact, there is more desulphurization when the matter of increased yield is considered. For example: Given a yield of 70 per cent coke by the beehive process and 75 per cent by the by-product process from coal carrying 1 per cent sulphur, the respective problems are as follows:

	Beehive Oven, Per Cent.	By-product Oven, Per Cent.
Sulphur in coal	1.000	1.000
Sulphur volatilized	0.428	0.428
Sulphur remaining	0.570	0.572
Sulphur in coke	0.817	0.763

So that the practical volatilization of sulphur from the beehive process is only 18.3 per cent, while in the by-product it is 23.7 per cent. In our own beehive practice we have always used 20 per cent as the amount of sulphur eliminated from all sources, figuring from coal to coke, this being the result of numerous laboratory and practical tests on the Connellsville coal.

Attention has been directed in the preceding paragraphs to the sulphur as pyrite. Let us look into the other forms that may be present in addition to the sulphide. Any organic sulphur present remains, for the most part, in the coke. It is readily seen how it

*From a paper prepared for the February meeting of the American Institute of Mining Engineers, New York.
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would be unaffected by aeration except in event of total destruction of the carbon itself, with which the organic sulphur is supposed to be combined.

Any sulphates present, such as CaSO_4 , would also be unaffected by aeration or superaeration in the beehive process; no amount of "airing" would help to eliminate the sulphur. We know of cases in which the sulphur in the resultant coke was as high, or even higher, as in the coal, from which it must be concluded that much of the sulphur was present in the coal as sulphate, or the so-called organic sulphur; or else the ash of the coal was rich in iron, lime and magnesia, for there is a dictum that it is never possible to produce a low sulphur coke from the coal the ash of which is high in these elements. Superaeration cannot and will not ameliorate these conditions.

Perhaps everyone is familiar with both the beehive and by-product oven practice in this country, quenching the coke by copious amounts of water. In the former case, it is customary to "water out" in the oven itself, while in the latter it is done externally by means of suitable quenching stations. In beehive practice, it takes approximately 1,000 gals. of water to quench a 5-ton charge of coke, consuming about three-quarters hour, either by hand watering with a hose, or with a sprinkler of the Stauff type, which is placed in the oven on top of the coke. The by-product practice is much quicker, but the external watering produces darker coke.

Theoretically, it would seem possible to remove considerable sulphur by the quenching process. We have already indicated how iron sulphide (FeS) is formed in the coking process. The action of the water on the sulphide is as follows: $\text{FeS} + \text{H}_2\text{O} = \text{FeO} + \text{H}_2\text{S}$, in which it is assumed that the coke is quenched externally. The odor of sulphuretted hydrogen is easily detected (but it will be appreciated that a little of this gas goes a long way), and the color of the coke, wherein rust spots appear, shows the presence of iron oxide. The practical coke burner is always suspicious of what he terms "rusty coke," as it invariably is an indication of high sulphur coke. The same holds true in quenching in the oven itself, as in beehive practice. Sulphuretted hydrogen (H_2S) is evolved, but, at the same time, the water as steam is decomposed by the carbon, $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$, which fact probably accounts for a part of the large percentage of carbon monoxide and hydrogen gas found in the gas from tunnels of beehive ovens, the water being formed from the combustion of the gases during the coking processes, which is virtually a low grade producer gas of the following composition:

	By Volume, Per Cent.
CO_2	3.0
CO	9.0
H_2	11.0
CH_4	0.3
N_2	76.7

The desulphurization of coke by water cannot be complete. The coke mass cools too quickly and its

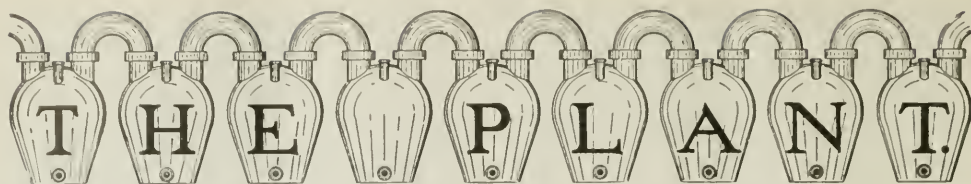
very structure prevents the rapid penetration of the water thrown on it, especially in the denser varieties. As the temperature is lowered the reaction involved becomes too slow to be of practical benefit. Data as to the exact amount of sulphur eliminated in this way are rather scarce, but our own experience, based on the general laws of volatilization set forth elsewhere, leads us to the conclusion that only an infinitesimal percentage of sulphur is thrown off during the quenching process. Laboratory and practical tests, in which the coke has been allowed to cool naturally, show but little difference in the sulphur content from those in which the coke has been quenched with water. Certainly there could be only a few hundredths of 1 per cent in favor of the water-quenched coke, at the most, in a coke averaging 1 per cent sulphur.

The prime object of the use of water is to lower the temperature of the coke for handling, not for desulphurization, and the quenching process should be so regarded. However, we are of the opinion that quenching by the by-product practice will eliminate more sulphur than by the beehive method, which may partially explain the greater total volatilization of sulphur in the former, elsewhere intimated.

It may not be generally known, in connection with the subject, that addition of muriatic acid (HCl) to the water greatly facilitates the removal of sulphur during the quenching process. The action of this acid on iron sulphide is positive at all temperatures, thus, $\text{FeS} + 2\text{HCl} = \text{FeCl}_2 + \text{H}_2\text{S}$. There was, of course, a time when the cost prohibited the use of this method, but with the depletion of our low sulphur coking coals this may, in the near future, be a factor in the elimination of sulphur.

The records of the State Mining Bureau of California show a production of coal in California as early as 1861. At that time it was one of the sixteen coal-producing states and, relatively, of some importance as a coal producer. During the later part of that decade and throughout the following decade the coal production of California exceeded 100,000 tons annually and reached a maximum of 236,950 tons in 1880. Since 1881 the production has been irregular, having been influenced chiefly, up to the beginning of the present century, by the imports of Australian and British Columbian coals, the receipts of Australian coals depending principally upon the wheat production and shipments from the Pacific Coast. Since 1900, however, according to the United States Geological Survey, with the great increase in the production and use of petroleum which began in that year, coal production in California has fallen off.

The shipments of chilled and frozen beef from Buenos Aires to the United States, according to invoices certified at the consulate general, decreased in value from \$15,738,776 for 1914 to \$8,601,245 for 1915.



ASH TESTS FOR PERCENT OF FILLER IN PAPER.*

By JOS. E. PLUMSTEAD.

The value of ash tests or test for the percent of filler retained in paper is without doubt recognized, to a certain extent, by every practical papermaker. Few papermakers, however, attach any more significance to an ash test than that the sheet in question has a certain number of pounds of clay, agalite, or other filler, per hundred pounds of paper. Nevertheless, it is a fact that tests made at different points through the papermaking process have proven or disproven some of the seemingly unexplainable problems that often confront papermakers, paper mill engineers and chemists.

In a paper mill chemical laboratory the final result of an ash test of a certain sheet from a particular machine is usually reported as percent retention of filler, and this result is reached in the following manner: An average sample of the filler used is drawn in the usual manner, and a small weighed portion placed in a crucible over a blast lamp and ignited to a constant weight, and from these weighings the percentage of volatile matter in the filler is calculated. A weighed sample of the paper to be tested for percent retention of filler is then taken and ignited in a crucible to a constant weight, and from these weighings the percent ash in the paper is calculated. From the following formula the amount of filler retained in the paper or the percent retention by the machine is found:

Pc

— equals percent retention by machine.

$F - V$

When—

Pc = Percent ash in paper sample.

F = Pounds of filler used per hundred pounds of paper produced by that machine.

V = Volatile matter in the weight F.

If greater exactness is desired a correction may be made for the ash in the fiber used or in constituents of the paper other than the loading material. This is, however, useless from a practical standpoint.

There are various causes, in the filler itself, in the method of beating and in the manner of running the paper machine, for a higher or lower percentage of retention in some cases than in others. In the filler, qualities which tend to give a higher percentage of retention are, a colloidal character, fibrous texture and

large particles. These qualities may be estimated by a chemist's judgment from microscopical comparisons, elutriation and rate of settling tests and aniline dye absorption tests. The extremes of these qualities may cause almost any variation in the retention of filler. A thoroughly beaten stock will retain much more filler than stock beaten a short time. As high as twenty points of difference between stock beaten three and a half hours and stock beaten six hours has been noted. There are several ways in which the machine tender may raise or lower the retention of filler. If the machine has a short wire the speed of the machine should be correspondingly slow, otherwise harsher treatment must be resorted to in order to remove the water, and the water will, in being forced through the sheet faster, carry with it more of the filler. The stock should be run to the machine at the heaviest possible consistence to allow for the most efficient reuse of the rich white water which has been forced through the wire. An escape of the white water means an inevitable drop in the retention. If it cannot all be used to advantage at different points in the process it can be settled and the sludge drawn off and reused at some point, either in the beater or in the beater stuff chest. The ream weight will largely influence the retention of filler and this fact should be taken into consideration when comparing ash tests of different sheets, thus, other conditions being the same, the retention of an eighty-pound sheet should be about ten points higher than a fifty-pound sheet.

The writer has found the following method effective in hunting down reasons for seemingly inexplicably low retentions. Convenient portions of stock, about 50 cubic centimeters, are taken from the beater or beater chest and the flow box and a dry sample from the reel, following as nearly as possible the transit of the stock from one place to the other. The wet and dry samples are then placed in a dry oven and dried to a constant weight and then ignited and weighed, and the ratio of filler to fiber noted in each case. These tests are repeated several times and the averages taken. The average ratios obtained in this manner are then compared with ratios obtained in the same manner on the same kind of sheet, running on the same machine or on another machine at conditions giving the recognized standard ash test for that sheet. These results should indicate the following things:

(1) Whether the required amount of filler was actually furnished to the beater.

(2) The consistence of the stock going on the wire.

*From Pulp and Paper Magazine.

(3) The comparative loss of filler through the wire.

With the trouble thus definitely located it is a simple matter to remedy the defect.

Occasionally in the run of routine ash tests when a small furnish of filler has been made per beater the retention will figure out more than 100 percent. This trouble can almost invariably be traced to a lack of system in furnishing broke to the beaters, either from furnishing broke in irregular quantities to different beaters of the same machine or furnishing the beaters of one machine with broke from another whose sheet contains a different relative amount of filler. It may be safely stated in the case of routine ash tests of paper of known qualities, if the retention varies more than five points either way from the average for that sheet, that machine trouble will have arisen in 75 per cent of the cases from irregularities in furnishing broke.

The writer has found that when all practicable precautions have been taken to prevent the loss of clay through escape of white water the approximate average retention for best English china clay is as follows:

10 lb. china clay used per hundred pounds paper made should give about 50 per cent.

15 lb. china clay used per hundred pounds paper made should give about 90 per cent.

20 lb. china clay used per hundred pounds paper made should give about 85 per cent.

This weight is made up of

Fibers	80%	= 1.2524 grammes
Loading material.....	15%	= 0.2348 grammes
Animal size.....	5%	= 0.0783 grammes

1.5655 grammes

and one cubic centimeter of paper contains

Fibers	0.783 grammes
Loading material.....	0.147 grammes
Animal size.....	0.049 grammes

0.979 grammes

As may be seen, in this case, the air space amounts to an important part—paper consequently possesses a not inconsiderable specific volume. This is lost in calendering, while a corresponding increase in the surface does not take place. The strength of the sheet is augmented by increasing pressure, but only up to a certain point, beyond which the strength again decreases. When the pressure in calendering is too high, therefore, the paper is rendered unnecessarily weak, but consideration for the foremost value, strength, is often not alone determinative; the paper must have a certain finish. The conditions noted have been fortified and confirmed by direct measurements and tests.

The proportion between the weight of the sheet and the volume, which, according to the foregoing, amounts to 0.979—consequently the weight of a cubic centimeter in grammes—is designated the apparent specific gravity, probably with reference to the air space, and is a dimension to which, certainly not without reason,

great importance is attached. According to former suppositions, it appears that the thickness of the paper must also be taken into consideration. This readily led to a step further and to the use of the strength of the surface unit of the cross-section, as a rule, in determining the solidity of a paper. The acceptance of such a standard is briefly stated customary in all material tests for similar purposes—also in stating the strength of special fibers—it has, however, obtained no established recognition but has been superseded, except in England or America, by the generally used tearing strength or breaking length—which, as is well known, is the figure representing the length at which a strip of paper, of the quality under consideration, that is hung up free, tears off at the point of suspension, owing to its own weight. The number which—moreover in harmony with the aforementioned cut-surface unit coefficient—has the advantage that it can be used directly, without regard to difference in the grammage weight, is most conveniently obtained with a Schopper apparatus, with a predetermined normal measurement of the strips of 180×15 millimeters whereby the average between the results of the machine and the cross-direction (in machine papers) can be decisively given. In the same manner, the strength of a single paper, per surface unit of the cross section, can be given: the question, however, is how far, in every instance, the accepted breadth and length is perfectly suitable for the test strips. An intelligent investigation may furnish an explanation of this.

In addition to the advantage of a unit of strength, uniform for different material, in using the section unit, we have the certainly not unimportant relation between the specific thickness of paper and its specific strength.

Between the two strength figures there is apparently a close connection. If we typify apparent specific gravity by S , fracture length by L , strength of the paper to the surface unit of the cross-section by K , thickness of the paper (as before) by t , and breadth of the test strip by b , the breaking load for the breadth $b = L \times b \times t \times S = K \times b \times t$, that means $L \times S = K$, or the product of the breaking length and the apparent specific gravity is the strength of the surface unit of the section. This proportion has been directly confirmed by careful experimental test in every instance and such an investigation is instructive and furnishes special knowledge as to the possibility of producing paper of great strength.

The aforementioned factors are the most important in what is known as the C.B.S. units. It would be difficult to predict to what extent the methods of determination indicated will find employment. In part they are only a development and another application of methods already in use, and up to the present time the new method appears to have attracted attention only in its home country. That it merits attention for certain questions and possesses more than speculative, theoretical interest, is probably far beyond any doubt.

THE PRODUCTION OF AMMONIA FROM CYANAMID.*

By DR. W. S. LANDIS.

After working for many years on the problem of the fixation of atmospheric nitrogen in the form of cyanides and cyanamids, the outbreak of the Boer War forced Professors Frank and Caro, of Berlin, to turn their attention to the utilization of their products otherwise than in the field of precious metal extraction. A consequence of the then existing economic situation was the discovery of the process of transforming the cyanamid compounds into ammonia. United States Patent No. 776,314, granted Nov. 29, 1904, most probably represents the first American publication on this subject.

According to the specifications of this patent various cyanamid compounds and derivatives, including the crude form of the calcium salt sold under the name of lime nitrogen, when treated with steam or water in the proportion of three molecules of water to two atoms of the nitrogen in the cyanamid salt, will yield ammonia. It is recommended in the specifications that the reaction be carried out at temperatures from 160°-180° C. in a closed vessel, though the claims of this patent cover temperatures above 100° C.

There has grown around this process and its later refinements in the last 15 years an extremely important ammonia industry. Naturally the greatest development has been in Europe, its home, and it is only within the past year that a plant comprising full size apparatus has been in operation in the United States. In attempting to catalog the various plants throughout the world which have been converting cyanamid into ammonia in large-scale operations, I find that available information, particularly since the outbreak of the European war, is so incomplete that the listing in consequence was very inaccurate. It is certain, however, that the transformation of cyanamid into ammonia is successfully carried out in Norway, Germany, France, Switzerland, Italy and Japan, and prior to the war in Belgium, the bulk of the product going into ammonium sulphate for the chemical and fertilizer trade. Norway is producing large quantities of ammonia used in the Birkeland-Eyde plants for the production of ammonium nitrate; France has produced considerable quantities of anhydrous ammonia by this process; at the present time Germany is producing enormous quantities of nitric acid from this cyanamid-ammonia by a newly developed oxidation process, and is erecting cyanamid plants equipped with ammonia apparatus at various places.

The fixation of atmospheric nitrogen, chiefly due to our Government's policy in respect to water power development, has not been practiced in the United States. During the year 1914 contracts were let in Germany by the American Cyanamid Co. for the

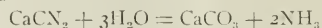
equipment of the largest single ammonia plant then projected or operating in the cyanamid industry, but the outbreak of the European war interfered with the shipment of this apparatus, nearly all of which was seized by the German Government for the purpose of providing for its own explosive requirements. It was possible to bring only a small portion of this equipment over to the states where it was set up and put into operation, and is now producing several tons of pure ammonia gas per day. This plant has been in continuous operation here for six months without any signs of trouble whatever and is considered to be most successful and satisfactory in every way.

The crude cyanamid or lime nitrogen is now a well known commercial product. The Canadian factory supplying the United States and its insular possessions with this product has a capacity of fixing nitrogen equivalent to 90,000 pounds of ammonia per day, and with the completion of certain additions now being made will be capable of supplying some 110,000 lbs. of ammonia each 24 hours. The demands for this product, most of which goes into the fertilizer industry, are so great that the plant is now operating at its full rated capacity. It is therefore evident that the supply of raw materials for an ammonia industry is in no sense limited.

Crude cyanamid, or lime nitrogen, the reagent used for the production of ammonia, is an electric furnace product, whose production has been described elsewhere by the writer. This material as turned out of the furnace contains nearly 25 per cent nitrogen in the form of CaCN_2 , 12 per cent CaO and 12 per cent carbon, with miscellaneous impurities derived from the various raw materials entering into its manufacture.

The other raw materials entering into the ammonia process are soda ash and hydrated lime. The quantities used are small, being approximately $3\frac{1}{2}$ per cent and 2 per cent respectively of the weight of lime nitrogen used. Steam and power requirements, which vary with the size of the plant, are discussed later.

On treating lime nitrogen with steam, ammonia is produced from the calcium cyanamid according to the following reaction:



The reaction is almost quantitative when carried out on a large scale according to the process to be described later in detail. This reaction is exothermic in character, and while the exact heat of formation of calcium cyanamid has never been determined accurately it is believed that the heat evolution from the decomposition of the cyanamid alone amounts to between 200 and 300 lbs. cal. per pound of ammonia evolved. This plays an important part in the present method of carrying out the process, inasmuch as after once starting the reaction under proper conditions it will proceed of itself, and, in fact, with such great velocity that only complicated and highly developed apparatus can take care of the gaseous products.

*From a paper presented at the 5th General Meeting of American Institute of Chemical Engineers, Jan. 12, 1916.

The process as carried out in the plant operating in the United States is essentially that described in the specifications of United States patent 1,149,633, dated Aug. 10, 1915, "Process of Making Ammonia from Calcium Cyanamid."

In order to take advantage of the exothermic character of the reaction, as above stated, the process is made to take place in an autoclave partly under high pressure. This apparatus consists of a steel tank approximately 6 feet in diameter, 21 feet high and capable of operating under a working pressure of 300 pounds per square inch. It is provided with a powerful stirring apparatus. Into this autoclave is charged about 12,000 pounds of mother liquor derived from a previous operation (fresh water to start), and lime nitrogen is slowly fed into this liquor under continuous agitation. As the lime nitrogen contains always a fraction of a per cent of undecomposed carbide, acetylene is evolved during this dissolving of the lime nitrogen.

A proper ventilating system is provided to remove this acetylene at such dilutions as will be non-explosive even if subjected to a source of ignition. The charging is usually carried on over a period of an hour so as to insure a thorough incorporation of the lime

the course of about 20 minutes with the relief valve open. The pressure then drops off slowly, as the gas is discharged, the rate of discharge being usually regulated by the attendant at the valve so as to maintain a constant pressure in the ammonia line, and at the end of about one and a half hours from the start of the operation the evolution has usually stopped. Nearly all of the cyanamid in the charge has been decomposed during the first period of the operation, but the solution is still highly charged with ammonia, which it is necessary to expel. A very small amount of undecomposed lime nitrogen may be left, particularly of polymerized forms, which yielded up ammonia only slowly. The steaming operating is then repeated, this time introducing steam until the pressure of the autoclave goes up to 6-8 atmospheres. The ammonia discharge valves are again opened until the autoclave is discharged, requiring a period averaging approximately one-half hour for this second discharge.

In order to insure practically complete evolution of all the ammonia in the autoclave it is advisable to again repeat the steaming to 6-8 atmospheres for a third period, discharging as before. During this last period of steaming and discharge rarely over 2 per cent of the total ammonia as charged is evolved, and

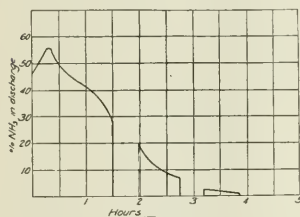


Fig.1

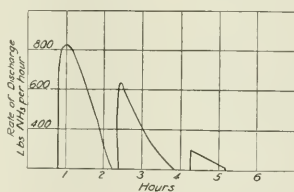


Fig.2

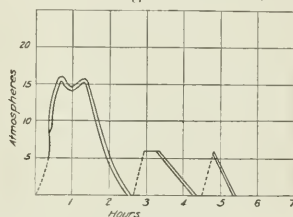


Fig.3

nitrogen with the solution and the breaking up of all lumps in the slurry. When the lime nitrogen has all been added to the autoclave the reagents—soda and lime—are added for the purpose of increasing the efficiency of ammonia evolution, principally through prevention of the formation of polymeric forms of cyanamid compounds which are difficult of transformation into ammonia.

The autoclave is then closed up and steam is admitted for approximately 15 minutes, or until the pressure gauge on the autoclave indicated three or four atmospheres, which shows that the temperature in the autoclave has been raised sufficiently to start the reaction at a fair rate of speed. The reaction then proceeds of itself, generating ammonia and steam in the autoclave, and it is necessary to relieve this gas accumulation by means of suitable valves to avoid excessive pressures in the apparatus. The rate of reaction becomes cumulative as the temperature rises, and this relief of ammonia and steam must be permitted.

Under normal working conditions the pressure in the autoclave will rise to about 12-15 atmospheres in

it can, therefore, be omitted if extraordinary demands on the capacity of the apparatus are made.

Extended studies of the course of this decomposition of lime nitrogen in the autoclave have been made both abroad and in this country, and are here reproduced in the form of charts. The discharge from the autoclave consists of a mixture of steam and ammonia, the composition progressively changing during the cycle. This variation in composition is shown for an actual operation carried out in this country in Fig. 1, in which the ordinates represent the percentage of NH_3 by weight in the ammonia-steam mixture discharged from the autoclaves, and the abscissa the time after start of the operation, analyses of discharge being made at approximately three-minute intervals.

The rate at which ammonia is discharged from the autoclaves under operating conditions varies with the imposed condition. It has been found that most requirements are met by discharging at such rate as to maintain a constant pressure of steam and ammonia in the main leading from the autoclaves. Under such conditions the rates of discharge during a given operating cycle are represented by the curve in Fig. 2, in

which the ordinates are the pounds of ammonia discharged per hour, and the abscissa again the various elapsed times from the start. In this case the charge in the autoclave was 7,000 pounds of lime nitrogen analyzing about 26 per cent equivalent NH_3 .

Where a uniform supply of ammonia is required it can be obtained by the insertion of a special type of gasometer in the system. Also suitable grouping of a number of autoclaves and cyclical operation of the same will assist greatly in obtaining a uniform rate of production without the use of such gasometer.

In Fig. 3 is shown a curve of the pressures existing in a European autoclave, slightly smaller than the one described above, and operating on a charge of 8,000 pounds of lime nitrogen. The dotted lines represent the admission of steam, and the full lines the pressures as shown on the gauge on the autoclave. The ammonia discharge valves of the autoclaves are opened where the lines are indicated double.

At the close of the operation the bottom discharge valve is opened and the mud contained therein runs by gravity into large suction filters of the well-known "Nutsche" type. Here the liquor is sucked off from the solid constituents, a thorough wash with water is given the sludge removed to the dump. Under normal operating conditions this sludge when dried contains less than 0.2 per cent of equivalent ammonia, and about 65 per cent of CaO in the forms of carbonate and hydrate. It is dark grey or black in color, due to the carbon present, and finds application as an agricultural lime. The liquor removed from the filter is used in dissolving the next batch.

In the manufacture of ammonium sulphate as carried out extensively abroad, the mixture of steam and ammonia coming from the autoclaves is led directly into an absorber and produces a high grade white sulphate. This production of sulphate is much simpler than from ammonia liquor. Where the introduction of the accompanying steam is not permissible, as in the production of certain ammonia salts which cannot be subjected to high temperatures, or where the process involves subsequent evaporation and crystallization, the ammonia-steam mixture coming from the autoclave is passed through a simple rectifying column provided with dephlegmator and condenser, and there is obtained therefrom a practically chemically pure ammonia gas, saturated with moisture at the temperature of the condensing water. This rectifying column is self-acting because of the large quantity of steam admitted with the ammonia-steam mixture, and requires no attention whatever in its operation, other than to shut off the cooling water to the condenser when not in use. The ammonia derived from the column, as before mentioned, is practically chemically pure, and is used directly in a large number of chemical industries. The Birkeland-Eyde engineers absorb this ammonia gas in distilled water, forming a dilute aqua ammonia, which they add directly to this

dilute acid for the manufacture of ammonium nitrate, the product being of extraordinary quality.

On the other hand, ammonium nitrate or equal grade may be produced directly from the ammonia gases dehydrated in the column without the water absorption step.

One of the large autoclave plants in France has been manufacturing anhydrous ammonia for years, and in addition to the above purification system they have installed an oil washer, charcoal filter and lime drying boxes before liquefaction. The oil washer, the writer was informed, was installed to remove some very minute traces of an unknown organic compound, but he has inferred that the character and quantity of this impurity, from the manipulation of this apparatus, is largely mythical.

For the production of nitric acid from ammonia, the product as taken from the condensers attached to the ammonia column is so pure that no trouble is occasioned by the poisoning of the catalyzers used in its subsequent oxidation.

I have with me assembled drawings of an autoclave plant of 16 autoclaves, such as supplied the Birkeland-Eyde Co., which is similar to those intended for this country. The rated capacity of the plant is 75,000 pounds of ammonia gas per day. The general arrangement of the apparatus, piping, etc., is clearly shown here by the use of colored inks, and I am sorry that photographic reproduction does not bring out the details of these drawings so that they can be shown in a more convenient form. Owing to the present inability to obtain this apparatus from Germany, where it has been manufactured on an extensive scale, the American Cyanamid Co. has redesigned the whole equipment, adapting it to American standards and manufacturing conditions, and is now building this equipment in the United States.

An extended study made by the writer a year ago on one of the European plants which had been operating for a long time, showed that the transformation efficiency of the nitrogen in the lime nitrogen into ammonia was over 99 per cent. Our American plant is showing operating efficiencies covering a period of several months substantially equal to the above.

An economical autoclave unit is one of eight working shells. As the operating load factor on these autoclaves is very close to 100 per cent it is not necessary to supply more than one spare shell to this eight autoclave equipment to insure a full 100 per cent load factor. Such a plant of eight autoclaves would require a 300 H. P. boiler. It was the old practice abroad to set the safety valve on the autoclave shells at 20 atmospheres and operate the boiler at this same pressure. In our own designs here in the United States we have successfully operated at 125 pounds steam pressure without trouble and can take steam from a common plant main. Superheated steam is preferable for the purpose, but not absolutely necessary. There is in addition required for operating the

lime nitrogen feeding device, the stirrers in the autoclaves, the vacuum pump and the air compressor, and miscellaneous sludge disposal equipment a continuous motor load of approximately 100 H. P. (the connected motor load would probably average about 200 H. P. depending upon local conditions).

In the compilation of a cost sheet for the production of ammonia from lime nitrogen there is such great latitude in unit costs concerned that the writer is presenting rather full quantitative data to which he is appending assumed unit costs. In most cases the assumed unit costs are averages existing before the outbreak of the European war, and to which an approximate return may be expected after its close. In any case they may be readily corrected to meet local conditions.

Lime Nitrogen.—26 per cent ammonia. It is unquestionably the cheapest source of nitrogen (ammonia) in this country. The sales prices are dependent to an extent upon the quantities and deliveries contracted for. The freight is allowed at \$3.00 per ton of lime nitrogen shipped in special containers, which should cover the greater portion of territory in the United States lying within a 500-mile haulage radius of Niagara.

Caustic Lime is to be air slaked on spot, 2 per cent weight lime nitrogen used assumed at \$6.00 per ton delivered.

Soda Ash.—3½ per cent of weight of lime nitrogen at \$16.00 per ton delivered.

Power.—100 H. P. continuous at 1 cent per H. P. hour.

Steam at 30 cents per 1,000 pounds, 60 per cent weight lime nitrogen.

Water.—2 U. S. gallons per pound of ammonia. As the larger part of this is used in condensers and coolers the greater proportion may be salt water. Assumed at 2 cents per 1,000 gallons.

Labor and Superintendence.—Assumed at 300 man-hours per day at 30 cents per man-hour.

Repairs and Renewals.—\$1.50 per ton ammonia, a record of long time operations.

Interest.—Assumed at 6 per cent on plant cost of \$120,000.

Depreciation.—On plant cost of \$120,000 depreciated in ten years, say 8 per cent.

On account of the varied building conditions existing throughout the country it is almost impossible to give a detailed estimate of the cost of plant. A recent projection of such costs made by this company for a plant of this size, from which I have deducted the cost of land, foundations and sludge disposal, shows that an ammonia plant of the size herein described could be erected for about \$120,000. This plant is designed to produce an ammonia gas as its final product cooled to the temperature of the available water of the condensers, and therefore not strictly anhydrous. This figure further assumes that water and power are fur-

nished the plant, and no provision is made for power or pumping plants.

Steel buildings with corrugated iron sides and roof, and of a type which have demonstrated themselves as fairly satisfactory for this service are included. The limitations imposed by building laws and choice of architecture may force one to materially modify this estimate, as cheaper forms of construction may be used. On the other hand, many may prefer a more elaborate type of building than provided in the above estimate, which would materially raise this figure.

OPERATING COST OF AMMONIA PLANT.

Capacity 30,000 lbs. Ammonia Per Day, Gas Saturated With Water at Cooling Water Temperatures.

Item.	Quantity.	Rate.	Per Day.	Per lb. Ammonia.
Freight		\$3.00	\$180.00	\$0.00600
Lime	120 tons	6.00	7.20	0.00024
Soda	210 tons	16.00	33.60	0.00112
Power	2,400 HP. hrs.	.01	24.00	0.00080
Steam	72,000 lbs.	.30	21.60	0.00072
Water	60,000 gals.	.02	1.20	0.00004
Labor	300 man-hrs.	.30	90.00	0.00300
Repairs and Renewals			22.50	0.00075
Interest			20.00	0.00067
Depreciation			26.66	0.00089
Miscellaneous			24.67	0.00082

Total conversion cost, excluding NH₃ losses\$451.43 \$0.01505

The large number of installations operating with perfect success in various parts of the world for a number of years have demonstrated the commercial possibility of making ammonia from lime nitrogen. The plant in its present highly developed state is extremely certain in its action and simple to operate. The efficiency obtained in the transformation of the nitrogen in lime nitrogen into ammonia gas is upwards of 98 per cent, or almost quantitative. The consumption of reagents is remarkably small, and they are cheap and easy to obtain in almost all parts of the world.

The quality of the ammonia produced by this process is not surpassed by any in the United States. It is chemically pure as produced and requires no further costly and tedious purification to render it available for the highest grade chemical products, or for the production of liquefied anhydrous. The actual cost of production of this high-grade pure ammonia on a considerable scale, which enables one to take advantage of the lower prices at which lime nitrogen is offered, brings high-grade cyanamid-ammonia into the market almost as cheaply as the more impure forms already found there, and very much cheaper than it is possible to obtain an equal quality of ammonia from gas-house liquor, the coke ovens, etc.

The American consul general at Rio de Janeiro, Brazil, reports under date of December 31, 1915, that the price of Para rubber has risen steadily from 4.3 milreis per kilo, in the middle of November, 1915, to 6 milreis per kilo on the date of writing. As a result, general prosperity exists throughout the Amazon Valley.

THE CRACKING AND DISTILLATION OF PETROLEUM UNDER PRESSURE.*

By BENJAMIN T. BROOKS, PH. D.

The great increase in the consumption of gasoline during the last decade induced the apprehension that a serious shortage of petrol, or gasoline, suitable for use in motor vehicles would result. This has recently resulted in a small flood of patents describing various processes which have for their object the conversion of the heavier and generally less valuable petroleum oils into gasoline. The public press does not even yet seem to be aware of the steady development which has been going on in the petroleum industry and which now enables us to say with certainty that no serious shortage of gasoline will ever inconvenience the automobile trade so long as petroleum of even the heavier grade is produced in anything like the quantity now being brought forth in the world's various petroleum-producing centers. Several independent groups of investigators have contributed to the solution of this problem, and, although this cannot be considered a closed chapter of industrial research, certainly more than the preface has been written, since more than one method has been shown to be capable of successful, commercial, large-scale operation.

The great economic importance of the problem is indicated by the following facts, here briefly presented in abstract form. A good index of available natural or primary gasoline is obtained by reference to the crudes which yield it. The world's production of petroleum since 1900 is graphically shown in Fig. 1. Attention should be called to the fact that the greatest increases in the production of crude have been in fields yielding heavy oil containing little or no gasoline, as is the case with Californian and Mexican oils.

In 1910 there were in the United States, as nearly as can be ascertained from the registration statistics, about 350,000 motor vehicles in use; in 1911 the figure given was 550,000; in 1912 this total had mounted to 990,700, and, by the end of 1914, 1,868,000 motor vehicles had been registered.¹ More accurate data are available, giving the number of automobiles manufactured in this country since 1903.

The economic aspects of the motor fuel question are more fully discussed by the author in a recent number of the *Journal of Industrial and Engineering Chemistry*.² The following represent the principal factors in the question of an increased supply of motor fuel and show that cracking methods for the manufacture of gasoline must become of increasing importance:

1. The supply of motor fuel can be nearly doubled by employing spirit of about 56° Be. gravity and constituting the entire distillate boiling below 200° C. from high-grade crudes yielding gasoline.

2. Natural-gas gasoline, made by cold compression of "wet" natural gas, may yield, in the United States, 500,000 to 600,000 barrels. If this is blended with heavy naphtha so as to produce a heavier mixture suitable for use in automobiles, the total increase available will be approximately 1,000,000 barrels, or less than 4 per cent of the production of "primary" gasoline distilled from crudes in the United States.

3. The shale oil industry is of no importance in this country, and in England is practically in a static condition, and increased amounts of motor fuel can hardly be looked for from this source.

4. If all the by-product coke ovens now operating, or nearing completion, in the United States were

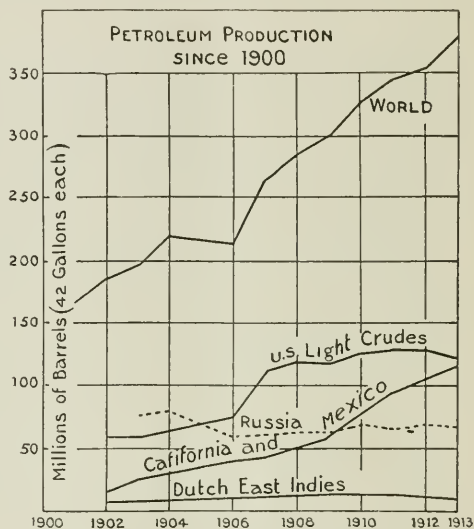


Fig. 1.

equipped with benzol recovery plants, the total production of benzol would be approximately 30,000,000 gallons (recovering 2 gallons of benzol per ton of coal). By the end of the present year about 7,600 by-product ovens will be in operation in this country.³

5. The price of 95 per cent alcohol for industrial purposes is normally 30 to 35 cents per gallon. This alcohol has only about 60 per cent of the calorific power of gasoline and has not been employed for motor fuel in England in normal times, when gasoline sold for 40 to 42 cents per gallon.

The earlier attempts to convert heavy petroleum hydrocarbons of high boiling-points into lighter, more volatile products were carried out with the object of increasing the yield of illuminating oil. But in very recent years the cracking problem has been attacked anew and with the object of increasing the yield of

*From paper presented at the meeting of the Section of Physics and Chemistry of the Franklin Institute held Oct. 7, 1915, and printed in the *Journal of the Institute*.

¹Oil, Paint and Drug Reporter, March 15, 1915. The Automobile for August, 1915, states that the registration statistics show that 2,070,900 cars are now in use in the United States.

²J. Ind. and Eng. Chem., 1915, 7, 177.

³Paving (Iron Trade Review, 1913, 625, 653) gives 6,200 by-product ovens in the United States at the end of the year 1913. If the number of by-product ovens becomes sufficient to supply the 40,000,000 tons of coke now consumed by our blast furnaces when they are working full capacity, we can reckon on a possible annual production of benzol of about 80,000,000 gallons.

gasoline, or motor fuel. The methods which have been employed to attain this end may be considered to be modifications of the following three general methods:

1. Heating heavy oil to cracking temperatures at atmospheric pressure.
2. Heating heavy petroleum oils to cracking temperatures under pressure.
3. Chemical decomposition effected by chemical reagents, such as aluminum chloride.

In discussing the first method, it should hardly be necessary to point out that the temperatures prevailing in the old cracking process for kerosene are not sufficiently high to produce greatly increased yields of gasoline. On the other hand, very high temperatures (*e. g.*, 900° C.) have been employed in the cracking of petroleum, as for the manufacture of Pintsch gas. In the latter process, about one gallon

pressed by the equation $\text{RCH}_2 - \text{CH}_2\text{CH}_2\text{R}_1 \rightarrow \text{RCH}_3 + \text{CH}_2 = \text{CH.R}_1$ —one might expect that the per cent by volume of unsaturated hydrocarbons would approximate 50 per cent of the product. However, separation of carbon and gaseous products, polymerization of the olefines, and formation of naphthenes occurs.⁵ I have found formaldehyde and formic acid among the products of the autoxidation of cracked oils, which fact may be considered as an indication of the presence of the methene group ($=\text{CH}_2$).⁶

It is, of course, obvious that, if hydrogenation could be carried out successfully in a commercial way, the customary treatment with sulphuric acid could be dispensed with. However, we have found that the ordinary desulphurization methods, even when most carefully carried out, apparently left traces of sulphur in the oil, so that, after comparatively very little use, the catalysts, both nickel and palladium, were rendered inactive.

In view of the recently-proposed method of Bergius, of hydrogenating without a metallic catalyst, an experiment was made in which a sample of cracked gasoline, iodine number 55.0, was maintained at 196° C. for 30 hours under a hydrogen pressure of 3,000 pounds per square inch. The iodine number of the gasoline, after the experiment, was 52.0, an effect probably accounted for by polymerization, since a similar reduction in iodine number was brought about in an atmosphere of nitrogen.

Since petroleum technologists have come to associate the characteristic, strong and unpleasant odor of cracked oils with olefines, and sometimes attribute the objectionable odor to their presence, it is worth while to note that highly-cracked gasoline, which had been treated with alkaline plumbite, or thoroughly desulphurized by copper oxide, had lost nearly all of its offensive, so-called odor of cracked oils. Metallic sodium is even more effective in producing sweet-smelling gasoline, although the percentage of olefines

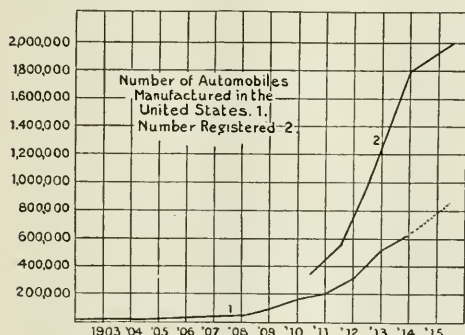


Fig. 2.

of light volatile liquid is obtained by compressing 1,000 cubic feet of the gas.⁴ A sample of this product, Sp. gr. 0.830, recently examined in this laboratory, yielded 88 per cent distilling below 115° C. It was a very highly unsaturated product, and when carefully treated with cold concentrated sulphuric acid this sample lost 48.0 per cent to the acid. The principal constituent of the remainder was benzol.

Experiments carried out in this laboratory show that at temperatures within the range 430° C. to 600° C., Solar oil, Sp. gr. 0.8862, yielded from 3 to 20 per cent of the gasoline boiling below 150° C. The gasoline so produced was highly unsaturated, the loss on treating with one-fifth volume of concentrated sulphuric acid averaging about 28 per cent. The presence of contact substances appeared to be without effect, except in the case of nickel, when the amount of gas produced was greater and the gasoline fraction of the resulting product showed a much greater loss to the sulphuric acid than when other contact substances were employed. A few of the experiments of this series are noted in the following, Table I.

If the cracking of a paraffin hydrocarbon is ex-

TABLE I.—Results of the Cracking of Texas Solar Oil at Atmospheric Pressure.

No.	Contact substance.	Per cent. boiling below 150° C.	Temperature Centigrade.	Time in hours.	Per cent. loss gas and coke.
1.	None	8.3	500°	0.5	8.7
2.	Pumice	8.8	420°	2.0	12.8
3.	Pumice	15.6	500°	2.0	17.5
4.	Nickel wire	12.3	500°	2.5	16.1
5.	Nickel wire	18.8	500°	5.0	16.5
6.	Nickel on Al ₂ O ₃ +H.	10.5	500°	2.5	15.1
7.	Nickel on Al ₂ O ₃ +H.	17.9	600°	2.0	30.8
8.	Copper on charcoal.	14.7	500°	2.0	13.1
9.	Copper on charcoal.	9.4	450°	6.0	12.0
10.	Copper gauze	14.1	500°	2.0	11.4
11.	Copper gauze	15.2	500°	2.5	11.8
12.	Copper gauze	18.8	500°	4.5	17.1
13.	Copper gauze +H ₂ O.	15.5	600°	2.0	11.1
14.	Iron	4.5	400°	2.7	...
15.	Iron+H ₂ O	8.6	450°	2.0	...
16.	Iron+H ₂ O	8.5	480°	3.5	...

⁵Engler and Gruning, Ber., 33, 1900, 2915. Engler and Lehmann, Ber., 30, 1897, 2367. Krämer and Spilker, Ber., 33, 1900, 2263. Nastukoff, J. Russ. Phys. Chem. Ges., 1904, 881.

⁶Cf. Wallach, Ann., 343, 1905, 34.

⁴Armstrong, J. Soc. Chem. Ind., 1884, 464.

remains unchanged. Pure olefines have a sweetish, agreeable odor. The odor of pure olefines or of cracked gasolines, which have been purified as by metallic sodium, while agreeable, is not exactly like the customary odor of gasoline, and, it might be said, neither is exceedingly pure normal heptane. Much to my surprise, I found that the cracked oils, desulphurized and otherwise purified by metallic sodium, held their water-white color and were very decidedly better, even in respect to odor, than good commercial "primary" gasoline, after the two samples had been exposed side by side to light and air for six months. The same marked difference was noted in the case of a sample of "primary" gasoline from Oklahoma crude, part of which was treated with metallic sodium and the second part "refined" by sulphuric acid in the usual manner. Sulphur compounds, perhaps in the sulphite condition, appear to catalyze the autoxidation of such refined oils, although Willstätter⁷ has shown that sulphur, in the form of the element at ordinary temperatures, does not accelerate oxidation. The offensive odor of cracked petroleum oils is due to small quantities of sulphur compounds, naphthenic acids, and basic nitrogen compounds, the latter probably of the pyridene type. Pure olefines slowly assume a pungent, disagreeable odor by autoxidation, peroxides, formaldehyde, formic acid and traces of other fatty acids, carbon dioxide, and resinous products being formed.

A number of processes have been patented which propose to hydrogenate the unsaturated hydrocarbons as they are formed, as by placing platinum or palladium in the cracking still. Others pass the oil vapors with steam through heated pipes, the claim being made that the steam and oil, or steam and carbon, react to give carbon monoxide and hydrogen, a claim which can undoubtedly be substantiated, if sufficiently high temperatures are employed. Another method, which is said to have been tried on a large scale, is that of passing the steam and oil vapors together over scrap iron at 540° to 650° C. Other processes propose cracking in the presence of nickel with or without steam. Another patentee employs oil and steam vapors over "red-hot" alumina, and another introduces coke into the oil-steam combination, an addition which those familiar with the cracking problem doubtless deem an unnecessary expedient. Our results with the steam-iron method indicate that hydrogenation of olefines under these conditions is not appreciable, and W. A. Hall⁸ has recently recorded experiences with the oil-steam-iron process which confirm our own. Hall states that he found steam totally inadequate as a means for preventing carbon deposits, and that "the extent of the hydrogenation was hard to determine, but, at all events, the spirit produced was so largely unsaturated that hydrogenation could not have been of much consequence, and, although we do not know what became of the small amount of

hydrogen evolved, we do know that the oxygen was sufficient to destroy completely the tubes in a surprisingly short space of time."

Another group of patents describes heating heavy oil under pressure, subsequently distilling at atmospheric pressure. The early experiments of Thorpe and Young,⁹ who heated paraffin under "a high pressure," obtaining a light oil which contained pentane, hexane, octane, and nonane, and the work of Ipatiew¹⁰ on the polymerization of ethylene, probably the most stable olefine hydrocarbon, and the work of Engler,¹¹ who showed that typical petroleum olefines could be converted into saturated naphthenes, induced us to follow up this line of work. Engler and Halmi¹² heated a heavy cylinder oil to 430° to 470° C. under 120 atmospheres pressure and by three successive treatments obtained 52 per cent boiling below 180° C., specific gravity 0.755. This method has also been described recently by Snelling,¹³ who employ 800 pounds pressure. In order to compare the results obtainable by heating under pressure and subsequently distilling at atmospheric pressure, we heated Oklahoma reduced oil, containing no constituents boiling below 275° C., for two hours under a pressure of 180 pounds per square inch, the pressure being that developed by its own vapors and decomposition products. We obtained 5 per cent gasoline by subsequently distilling at atmospheric pressure. In another experiment in the same apparatus, with the same quantity of reduced oil and also of two hours' duration and 180 pounds pressure, we obtained 30 per cent of gasoline by distilling the gasoline as fast as formed.

Little light, if any, can be thrown on this matter by attempting a mathematical discussion of the equilibria in such so-called systems. Suffice it to be said that according to familiar principles of equilibria, which we may qualitatively apply for the purpose of explanation, this difference, noted above, is evidently due to the fact that the gasoline hydrocarbons themselves are decomposed and, to obtain maximum yields, should be removed from the source of heat or sphere of reaction. Also, if the lighter, more volatile products are removed as fast as formed, the heavy residual matter in the still becomes continually hotter. This is shown by the following temperature curve obtained during distillation of Oklahoma reduced oil under 100 pounds pressure, the temperature being recorded by a thermo-couple in the oil several inches from the still bottom (see Fig. 3).

Operating by the Snelling method, the temperature within the still becomes lower and lower, if constant pressure is maintained, due to the accumulation of gases and volatile products in the still. This must have the result that the more stable hydrocarbons are not cracked. The emphasis Snelling places on the

⁹Chem. News, 1871, 23, 124; 1872, 26, 35.

¹⁰Ber. d. deut. chem. Ges., 1911, 44, 2973.

¹¹Ibid., 1900, 33, 2915; 1909, 42, 4610, 4613, 4620; 1910, 43, 338.

¹²Ibid., 1910, 43, 397.

¹³Bull. Am. Inst. Mining Engineers, 1915, 695.

⁷Ber., 1914, 2801.

⁸Engineering, 1915, 250; J. Gas Lighting, 1915, 455.

ratio of the volume of the charge to the total volume of the still obviously is to be interpreted that, if one were to fill the still nearly full, one could easily attain excessive and dangerous pressures, such as the 800 pounds mentioned by Snelling, before temperatures sufficiently high to crack the oil would be reached. If the still is charged with only a relatively very small quantity of oil, say one-twentieth volume, the whole

which are also described in considerable detail by Engler.²⁰ Laing²¹ also recommended the employment of 80 pounds pressure for carrying out cracking distillation of heavy petroleum.

On operating under pressures higher than those mentioned, we obtained continually increasing yields of gasoline up to about 250 pounds per square inch, when the yield diminished with further increase of pressure, the relative amount of coke and gas formed rapidly increasing beyond this point. The marked influence of pressure upon the percentage of olefines in the gasoline produced is also shown graphically in Fig. 4.

This decrease in the percentage of olefines in the resulting gasoline is undoubtedly due to their polymerization, not to hydrogenation, although Ipatiew observed that, in the distillation of petroleum under pressure, the evolved gases become continually poorer in hydrogen as the pressure is increased, in spite of the higher temperatures required to maintain the higher pressures. At a given temperature it is obvious that increase of pressure would tend to prevent dissociation with the formation of gaseous products. Engler²² obtained no hydrogen from kerosene by heating to temperatures below 470° C. Uebbelohde and Woronin²³ showed that, in the presence of nickel, hydrogen was dissociated from a Baku crude oil at as low a temperature as 180° C. In view of the re-

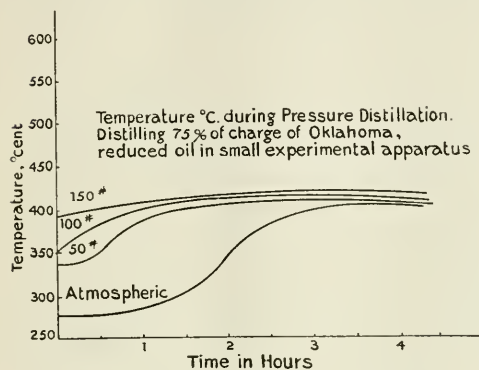


Fig. 3.

of it might easily be converted into gas and coke without producing the said pressure.

A modified form of the process of heating oil under pressure and subsequently distilling at atmospheric pressure has been patented by Testelin and Renard,¹⁴ who describe heating oil in pipes to temperatures not exceeding 450° C. and maintaining "sufficient pressure on the oil to keep it in the liquid state." Clark¹⁵ varies this by pumping the oil through heated pipes and passing the hot oil into a receiving drum, where distillation of the lighter products can take place. One object of the Clark method appears to be to minimize the deposition of coke in the heated pipes by the rapid passage of the oil through them. The Clark patent seems to be practically the old method of Benton, except that Benton permitted the lighter products to distil by release of the pressure.

In the course of our work on the distillation of heavy petroleum oils, in most cases Oklahoma reduced oil 30° Be., we have operated up to working pressures of 450 pounds per square inch. Young¹⁶ employed 10 to 20 pounds per square inch. Dewar and Redwood¹⁷ described distillation of heavy oils under pressure, but failed to state what pressure and did not indicate that the conditions of their method favored the production of gasoline. Boteg¹⁸ recommended four to six atmospheres for "illuminating oil," and Krey¹⁹ described the results of distilling oil under pressures of three to six atmospheres, the results of

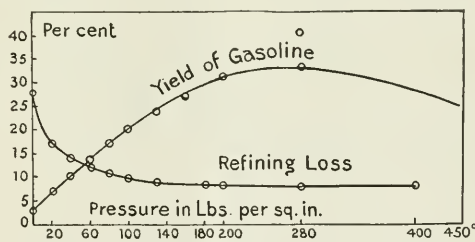


Fig. 4.

sults, quoted in Table I, I did not consider that cracking petroleum in the presence of nickel, even under pressure, was likely to give a satisfactory product. Sabatier and Mailhe²⁴ propose to make highly unsaturated gasoline by cracking in the presence of red-hot nickel and subsequently hydrogenate the resulting product. Hall²⁵ cracks oil in the form of vapor at 600° to 650° C. in the presence of nickel and under 50 to 75 pounds pressure, and obtains a highly unsaturated product, but very rich in benzol and its homologues. The effect noted by Ipatiew is evidently that of pressure on the character of the dissociation of the hydrocarbons. We have analyzed the gases evolved during distillation of Oklahoma reduced oil

¹⁴English Patent 3413, Feb. 10, 1913.

¹⁵U. S. Patent 1,119,496, Dec. 1, 1914.

¹⁶English Patent 3345, Dec. 27, 1865.

¹⁷U. S. Patent 419,591, 1890; 426, 173, 1891.

¹⁸Chem. Rev., 9, 1898, 24.

¹⁹German Patent 37,728, 1886.

²⁰Ber. d. deut. chem. Ges. 30, 1897, 2919.

²¹English Patent 11,757, 1890; 260,858, 1911.

²²Das Erdöl, I, 574.

²³Petroleum, 1911, 7, 9.

²⁴U. S. Patent 1,124,333.

²⁵English Patent 17,121, 1913.

at 110 pounds pressure and find that the percentage of hydrogen in the evolved gases is extremely small.

TABLE II.—Gases from Cracking Distillations Under 100 Pounds Pressure.

Sample No.	(a) From Jennings crude.			(b) Paraffin.		
	I	II	III	I	II	III
Temperature in still	340°C.	415°C.	422°C.	417°C.	432°C.	437°C.
CO ₂	1.2	0.5	0.0	0.0	0.0	0.0
CO	1.2	0.5	1.3	0.0	0.0	0.0
Aluminants	15.1	15.3	13.0	25.4	37.0	33.5
Hydrogen	0.0	4.0	4.4	0.3	0.9	3.0
Saturated hydrocarbons	81.5	79.7	81.3	74.3	62.1	63.5

Another noteworthy fact brought out by the above table is that higher temperatures are required to "crack" paraffin than a mixture of the cyclic hydrocarbons or naphthenes as represented by the Jennings oil. Paraffin is also more stable toward aluminum chloride than naphthenes of about the same range of boiling-point.

The increased yields obtained above 100 pounds and the smaller percentage of olefines in the product constitute the basis of United States patent No. 1,101,482. The results quoted in Fig. 4 were obtained in a small laboratory apparatus and do not represent the maximum yields obtainable, nor the highest quality of product. The ratio of heating surface to the volume of oil in the still affects markedly the rate at which cracking distillation can be carried out. Were the process merely one of distillation, this would seem too obvious to mention. However, the *cracking* of the oil apparently occurs chiefly at the heated surfaces, where the heat is supplied to the oil, and considerable time must be allowed for the oil to be cracked to the lighter hydrocarbons and *too rapid distillation prevented*, as by slow firing and refluxing the heavier fractions back into the still. *Slow* and less intense firing of the still also has the result of greatly diminishing the percentage of olefines in the gasoline produced, although the yield of gasoline is much increased.

We have found that the amount of gas evolved and coke deposited increases very rapidly as the working pressure is increased beyond 100 pounds. This figure varies considerably in different apparatus and with different distillation rates. Small laboratory apparatus gives more coke and gas and more highly unsaturated gasoline than large apparatus. The rate at which gas is given off during distillation of a given charge of oil at constant pressure is greatest during the coking stage, i. e., after 85 per cent of the charge has been distilled—a procedure naturally not carried out in practice. This is shown by the curves in Fig. 5.

The percentage of coke deposited also varies greatly according to the form of the apparatus and the method of operating. Thus very little coke is deposited in an ordinary horizontal still during distillation at 100 pounds, if not more than 60 per cent of the charge is distilled. This will naturally vary greatly with the character of the oil charged into the still. With clean paraffin distillate in a still of the Burton

type, the amount of coke deposited in 24 hours from 200 barrels charge rarely exceeds 125 pounds. We have found that, if the heating surfaces are vertical, the quantity of coke deposited is not more than one-fifth as much as is obtained under the same conditions but with the heating surfaces horizontal, as on an ordinary still bottom. If the distillation is not carried out beyond 60 per cent of the charge, a large part of the coke remains suspended in the residual oil as gritty, sandlike particles.

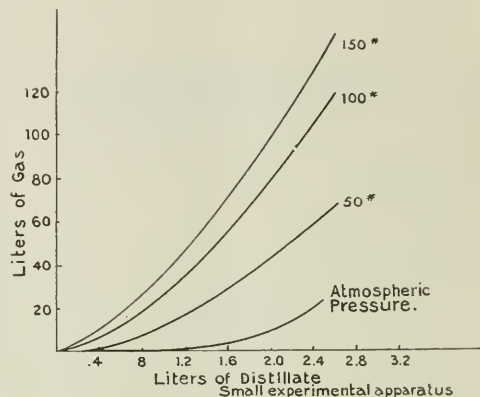


Fig. 5.

We have made use of the above-mentioned facts by so operating²⁶ that the heating surfaces are vertical, maintaining a large ratio between heating surface and volume of oil charged and removing the sandlike coke particles, by gravity and flow of oil through the apparatus, into a cooler zone, which prevents their cementing together in the form of a hard, compact mass. Another patentee²⁷ places false bottoms in horizontal cylindrical stills, which collect much of the coke that would otherwise deposit on the hot bottom.

We are unable to confirm the claims made by Burton to the effect that condensing the vapors under 75 pounds pressure yields gasoline of saturated character, whereas releasing the vapors close to the still and condensing them at atmospheric pressure yields gasoline of too unsaturated character for industrial use. By distilling Oklahoma reduced oil under 80 pounds pressure, we obtained by both methods products which were practically identical in this respect.

Gasoline:	Vapors condensed under	
	80 pounds pressure.	Atmospheric pressure.
Per cent. refining loss to 5 per cent. concentrated H ₂ SO ₄	7.9	8.0
Per cent. refining loss to 5 per cent. fuming H ₂ SO ₄	12.2	12.0
Kerosene:		
Per cent. refining loss to 5 per cent. fuming H ₂ SO ₄	9.0	8.0

²⁶U. S. Patent 1,131,309.

²⁷Humphrey, U. S. Patent 1,122,000; 1,122,003, 1914.

The very slight change resulting from heating a cracked oil, iodine number 55.0, for 30 hours at 196° C. under a hydrogen pressure of 3,000 pounds per square inch, certainly indicates that polymerization of petroleum olefines does not occur to an appreciable extent below 200° C. The experiments of Semmler²⁸ on the polymerization of isoprene, myrcene, and other hydrocarbons by heating under pressure are interesting in this connection. The polymerization of butadiene derivatives by heat and pressure occurs much more readily than is the case with other olefines, at least so far as known. By heating myrcene four hours at 250° to 260° C., Semmler obtained a 50 per cent yield of the diterpene $C^{20}H^{32}(F^3)$. It should be noted that the product is still highly unsaturated, containing three double bonds. It is my opinion that during the distillation of petroleum oils under pressure polymerization of the olefines formed occurs in the still proper, where higher temperatures, 380° to 420° C., prevail, not, as claimed by Burton, in the water-cooled, condenser coils, where much lower temperatures are the rule. We are now engaged in studying the question of polymerization of olefines by heat and pressure at regular temperature intervals above 200° C.

However, the successful manufacture of gasoline on a large scale by cracking heavy oil under pressure was first carried out by Burton and his associates at the Whiting refinery of the Standard Oil Company. Although the arrangement of Burton's apparatus is essentially the same as that of Dewar and Redwood, and the pressure employed by him, 75 pounds per square inch, was employed previously by others, Burton demonstrated that such distillation could be safely carried out on a large scale.

Several years ago we carried out experiments on the cracking of oil in the form of vapor under various pressures. After working with a semi-large unit, a still 20 feet long and 30 inches in diameter, under pressures up to 275 pounds per square inch, we believed that the danger from explosion could be considerably lessened, if the oil could be passed continuously in the form of spray or vapor through a suitable apparatus, so that the amount of liquid oil under heat and pressure at any moment would be relatively small. In view of the fact that this process has now become rather well known, I shall not go into detail further than to state that, except when the temperature was very carefully controlled, the deposition of coke was greater than when the apparatus contained liquid oil under the same pressure. Regulation of the pressure by permitting the gaseous products to accumulate or by introducing gas, such as hydrogen or water gas, is also a factor. Heavy oil cannot be completely vaporized at any except very low pressures. With the heavier oils, cracking begins at once when vaporization is attempted. Tar or coke particles coming into contact with the heated walls of the apparatus

become cemented there, whereas when filled with oil the rather violent motion of the oil in ebullition tends to entangle and carry away the coke particles, and the heavy residue, carrying as much as 15 per cent of sandlike coke, depending upon the conditions of operation, is slowly swept out of the apparatus when operating on the continuous system as we have done, or is caught on the false bottoms provided for the purpose in the Burton-Humphries method.

We have examined the gasoline made from Oklahoma reduced oil, 30° Be., by distilling under 100 pounds pressure, and find that, in addition to approximately 8 per cent of benzol, toluol, and metaxylol, the gasoline appears to consist chiefly of normal paraffin hydrocarbons.²⁹

The public press has recently given a great deal of space to the possibility of manufacturing benzol and toluol by cracking petroleum vapors, at temperatures

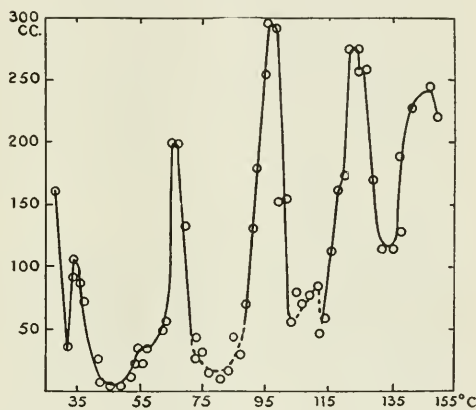


Fig. 6.

within the range 600° to 650° C. and under 75 pounds pressure. A communication to the author from W. A. Hall states that a large plant, erected at Thames Haven, England, has been taken over by the government for the manufacture of benzol and toluol, employing as a raw material the ordinary fuel oil used in the British navy. Mr. Hall says: "I can state that the spirit derived from this cracking operation contained 22 per cent of C. P. toluol, as determined by Sir Boverton Redwood, who has had the whole matter in charge."

The formation of aromatic hydrocarbons from petroleum oils has heretofore been assumed to be due to complex and little-understood changes, such as dehydrogenation of naphthenes and the formation of acetylene, and the condensation of the latter to benzene and its homologues.

We have found the above-named aromatic hydrocarbons in gasoline made by cracking heavy Oklahoma reduced oil under a pressure of 100 pounds per square

²⁸Ber. d. deut. chem. Ges., 1913, 1569.

²⁹Experimental work done by I. W. Humphrey.

inch. Treatment of the gasoline so obtained by liquid sulphur dioxide gave 10.0 per cent of olefines and aromatic hydrocarbons, which mixture was fractionated several times, and the fractions whose boiling-points corresponded to the boiling-points of benzol, toluol, and xylol were nitrated in the usual manner, water added, and the crude crystalline mass thus obtained recrystallized several times from alcohol. We obtained in this way 1-, 3-dinitrobenzol, melting-point 90°C .; also 2-, 4-dinitrotoluol of melting-point 70°C . and 2-, 4-, 6-trinitrometaxyol, melting at 182°C .

Since relatively little gas is evolved when distilling under 100 pounds pressure, and since the gas evolved contains not more than 4.4 per cent hydrogen, it appears highly improbable that the aromatic hydrocarbons in question are produced, either directly or indirectly, by a process of splitting off of hydrogen. Since benzol and a few of its simpler homologues have been found in all petroleum which have been thoroughly examined, I believe that the occurrence of benzol, toluol, and xylol in the gasoline made by cracking heavy oils under the conditions described above is to be explained by the splitting or "cracking" of high-boiling complex hydrocarbons,³⁰ containing the phenyl radicle, for example, such as $\text{C}_{16}\text{H}_2\text{C}_{10}\text{H}_{18}$, which would be the empirical formula for a phenyl derivative of the naphthene $\text{C}_{10}\text{H}_{20}$.

Further evidence in support of this hypothesis is found in the fact that gasoline made by cracking Oklahoma reduced oil by anhydrous aluminum chloride contains a relatively large percentage of benzol, toluol, and xylol. It is known that the higher benzol homologues are broken down by aluminum chloride. A hydrocarbon of the type $\text{C}_6\text{H}_5\text{C}_{10}\text{H}_{21}$ would therefore be expected to yield a mixture of decomposition products containing a small percentage of benzol. One liter of the gasoline made by cracking with AlCl_3 was extracted four times with liquid sulphur dioxide, one pound being employed for each successive extraction. The gasoline was cooled to -15°C . and thoroughly shaken with the liquid sulphur dioxide in a large Dewar flask. From one liter of this gasoline we obtained 325 c.c. soluble in liquid sulphur dioxide, which yielded the following:

Fraction.	Volume.	Result of nitration.
$45^{\circ}\text{--}90^{\circ}\text{C}$.	75 c.c.	3.6 g. dinitrobenzol
$90^{\circ}\text{--}120^{\circ}\text{C}$.	85 c.c.	13.8 g. dinitrotoluol
$120^{\circ}\text{--}145^{\circ}\text{C}$.	55 c.c.	39.6 g. trinitroxyol

This hypothesis is further supported by our finding that pure paraffin, on cracking by distillation under 100 pounds pressure, yields gasoline free from benzol

hydrocarbons, and, on the other hand, synthetic phenyl-paraffins are broken down by cracking, as in pressure distillation or by heating with aluminium chloride, giving benzol and its simpler homologues among the reaction products.

The phenyl paraffin was prepared by chlorinating ordinary white commercial paraffin until the gain in weight was equivalent to that required by the formation of the monochloride, the paraffin being considered as a mixture of hydrocarbons of the mean molecular weight corresponding to $\text{C}_{24}\text{H}_{50}$. This chlorinated product was dissolved in about four times the quantity of benzol required by the reaction and treated with 7 per cent anhydrous aluminum chloride at room temperature. After standing six hours the mixture was warmed to 80°C ., until HCl was no longer evolved. The excess benzol was completely removed by distillation with steam, and the product separated from water and dried. To 500 grammes of this product 35 grammes anhydrous of aluminum chloride were added and the mixture strongly heated for four hours, the reaction product being partly refluxed back into the distilling flask. On rectifying the distillate, 55 c.c. of benzol, boiling-point 78° to 85°C ., and 11 c.c. of toluol, boiling-point 105° to 115°C ., were obtained, which products were further identified by conversion into the dinitro-derivatives.

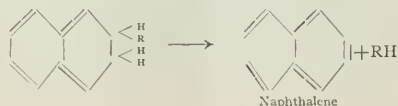
Two and one-half kilos of the synthetic phenyl paraffin, from which free benzol had been carefully removed, were subjected to distillation at 75 pounds pressure during a period of three hours. The distillate, 1,500 c.c., was fractionated, and the fractions, 70° to 100°C ., 100° to 115°C ., and 115° to 145°C ., examined for aromatic hydrocarbons by nitration.

Fraction.	Volume in c.c.	Grammes dinitro-derivative.
$70^{\circ}\text{--}100^{\circ}\text{C}$.	112	25 dinitrobenzol ³
$100^{\circ}\text{--}115^{\circ}\text{C}$.	150	40 dinitrotoluol ³
$115^{\circ}\text{--}145^{\circ}\text{C}$.	272	

There are, of course, other conditions in which aromatic hydrocarbons are formed by complex reactions which take place at much higher temperatures. Such conditions obtain in the Hall process carried out at about 650°C ., and in the manufacture of Pintsch gas at about 900°C . Abundant evolution of gas and separation of carbon occur under these conditions.

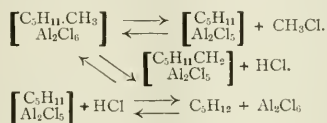
When heavy petroleum oils are heated with anhydrous aluminum chloride, cracking occurs with the formation of gaseous hydrocarbons and gasoline and kerosene, and, if the higher boiling oils are refluxed back into the still, yields of 15 to 25 per cent gasoline may be obtained, depending upon the conditions. This process has been recently patented. The gasoline made by this process is practically free from unsaturated hydrocarbons. Most of the sulphur present in the original oil is evolved as hydrogen sulphide, which may be removed from the distillate by washing with alkali. The gasoline so made is very sweet in odor and very stable to light and air. I have found that the characteristic odor of most commercial gaso-

³⁰Jones and Wheeler (J. Chem. Soc., 1914, 2562) have shown that hydrocarbons of the aromatic series are produced in the distillation of coal at 350°C ., or below the temperatures at which hydrogen is split off. They suggest that aromatic compounds may be formed by reactions such as the following:



line is in part due to traces of naphthenic acids, which may be isolated as the sodium soap by treatment with metallic sodium. The aluminum chloride gasoline is free from this odor; in fact, we have found that ordinary gasoline to which 2 per cent of Russian naphthenic acids were added was completely deodorized by slowly distilling with aluminum chloride.

In the cracking of hydrocarbons with aluminum chloride the nature of the reaction is obscure. The formation of definite compounds of hydrocarbons with aluminum chloride has been shown repeatedly. In view of this fact, and also that free hydrogen chloride (or hydrogen bromide when aluminum bromide is employed) is claimed to facilitate the cracking of certain hydrocarbons, the following series of reactions have been proposed to account for the phenomena:



It has been shown that in the practice of the method for the manufacture of gasoline the coke, which is formed in relatively large amount, may be kept scraped free from the still bottom by a mechanical stirring device.

By way of *résumé*, it should again be pointed out that, while a very large number of patents have been granted describing processes for the manufacture of gasoline from heavy petroleum oils, it should be borne in mind that it is almost impossible to decompose heavy petroleum oils without the production of more or less low-boiling hydrocarbons, no matter what method is employed, provided a suitable temperature, say 380° C. to 450° C., prevails somewhere in the series of operations. The chief difficulty in large-scale operation is the deposition of coke. In view of the public and private history of many so-called discoveries in this field, the heralding of any one process as being the best would at this time be premature. Undoubtedly several years must yet elapse before anything like a standard practice will have been evolved, and that company having had the most experience with large-scale operation will, by the various improvements introduced as a result of persistent, patient trial and experience, undoubtedly dominate the field for longer than 17 years.

The U. S. Civil Service Commission, Washington, D. C., will hold an open competitive examination for analyst, for men only, on March 8, 1916. Salary ranges from \$800 to \$1,020 per annum. The duties of this position will consist in making routine analyses of coal, calorimetric experiments, and analyses of ores.

New zinc refineries have been started in Japan since the war started, the *Japan Times* states, because of difficulties that have been met by importers.

UTILIZATION OF SOUTHERN WOOD WASTE.*

By ARTHUR D. LITTLE.†

Mark Twain says, "We all talk about the weather, but nothing is done." So it is with wood waste utilization. The lumbermen are interested, of course, but their interest is tempered by weariness and restrained by skepticism. They are open to conviction but would like to see anyone who can convince them. Much the same situation may be found where any of our great industrial wastes are concerned. Those who are responsible for the wastes are so close to them and so long familiar with them that they have come to regard them as the unavoidable accompaniment of the industry. Moreover, plans for waste utilization commonly involve the extension of a business into regions which, however familiar they may be to those doing business in them, are new and strange to the makers of the waste. Conversely, those whose specialized experience might enable them to utilize the waste to advantage, hesitate to incur the large capital expenditure required for establishing an industry dependent upon a raw material over which they have no control and the supply of which may cease at any time, as, for example, when a lumber mill burns down.

These are real and serious obstacles in the way of the utilization of wastes, but the things which anyone can do easily bring no great rewards. The world belongs to those who overcome difficulties and nowhere does it offer richer promise of potential wealth made actual than in the colossal wastes of lumbering.

The figures involved are of astronomical proportions and consequently make little more impression on the mind than the distances of the fixed stars. Let us, however, try once more really to comprehend them. On a total annual cut of fifty billion feet board measure of merchantable lumber, at least seventy-five billion feet, or about 112,000,000 tons, of wood waste are produced. For every man, woman and child in the country there is therefore annually wasted more than a ton of wood.

The proportion of waste to merchantable lumber varies within wide limits with the kind of wood. In the lumbering of hardwoods, according to Goodman, only 15 per cent of the weight of the standing timber appears as finished lumber. Sixty-five to seventy per cent of the original tree is left on the ground and the mill waste amounts to over a cord per 1,000 ft. of lumber. Frankforter, who had exceptional opportunities for studying the lumber industry in the middle, northern and western states, reports that in these sections of the country the best equipped and most skillfully operated mills utilize a little less than 40 per cent of the total weight of wood in lumber, lath and shingles. Our own large scale studies on longleaf yellow

*Address before the 8th Annual Meeting of the American Institute of Chemical Engineers, Jan. 12 to 15, 1916.

†Arthur D. Little, Inc., Boston, Mass.

pine have proved that under the best operating conditions only 33.42 per cent of the average tree becomes available as lumber, box shooks, lath and shingles; two-thirds is wasted. In the estimate of total annual waste given above an average of 60 per cent of the entire tree was reckoned as waste but in view of the loss on yellow pine, which is our most important timber tree, and the far greater proportionate loss on hardwoods, it is evident that the total annual waste is substantially more than seventy-five billion feet and may even reach ninety billion feet. Frankforter's estimate of 100 billion feet on a smaller annual cut is undoubtedly too high and not in accordance with his other figures.

Of all our timber trees none lends itself more readily to waste utilization than longleaf yellow pine. It is cut more largely than any other species and the individual operations are commonly on a great scale which ensures the local concentration of waste in vast amounts. For these reasons and because my associates and I have studied the waste utilization problems presented by this wood more carefully than those of any other species, I shall ignore hardwood distillation, the use of extracted chestnut chips for pulp and paper making, and the occasional use of mill waste from northern conifers in sulphite pulp mills, and ask you to direct your attention solely to the utilization of wood waste from longleaf yellow pine.

The present annual cut of this species is about fifteen billion feet, board measure. The waste is equivalent to thirty billion feet. It may be said at once, without fear of successful contradiction, that the potential profits in this waste are far greater than any actual profits which this branch of the lumber industry can be made to yield from lumber. When this waste is intelligently considered, not as waste but as raw material, it will be seen to afford a basis for building up the greatest group of correlated by-product industries the world has ever seen. The products of these industries will comprise woodpulp, pulpboard, paper, paper bags, paper twine, turpentine, rosin, pine oil, charcoal, tar, ethyl alcohol, cattle feed, varnishes, ether and not improbably acetic acid, wood alcohol, acetone and producer gas.

The wood of longleaf pine is heavy, exceedingly hard, very tough, coarse-grained, compact, durable and very resinous. Its density varies with the height from the ground, the age of the tree and its content of pitch or oleoresin. Sargent gives the average specific gravity as about 0.7, which would seem to be too high; determinations in the Forest Products Laboratory ranged from 0.426 to 0.583. Determinations in our own laboratory gave 0.626 as the specific gravity of round wood averaging seven inches in diameter. The weight per cubic foot for logging waste we found to be 39.1 lbs. bone-dry. The weight per cord depends greatly upon the shape and size of the pieces. On the dry basis we have found the sawdust to weigh about 1,400 lbs., mill waste with little or no bark 2,340 lbs., with

much bark 1,708 lbs.; logging waste in the form of fairly smooth, round logs weighs about 3,260 lbs., and if rough and irregular will average 1,860 lbs., while mature longleaf pine consisting largely of heartwood will run about 4,300 lbs. to the cord, bone-dry.

We find the ultimate composition of longleaf pine to be:

Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur	Ash	Total Per Cent
53.96	7.13	38.65	0.03	0.01	0.16	100

Our determination of fuel value of average sawmill dust gave 9,240 B. t. u., dry basis. Moisture in green wood averages 34.15 per cent, fresh green stumps average 28.60 per cent, lightwood 13.35 per cent. Stumps about six years old carry around 20 per cent of water and kiln-dried lumber contains an average of about 10 per cent. The proportion of bark varies to some extent with the age of the tree and is relatively high. Small, round Mississippi wood had about 9 per cent, Florida pulpwood upward of 11 per cent, and Florida trees over 18 inches diameter bore 8.6 per cent of bark by weight. Determinations in our laboratory of the fiber length of longleaf pine gave a maximum of 7.40 mm., minimum 3.00 mm., with an average of 4.60 mm., as compared with 3 to 3.5 mm., for spruce.

In determining the amount of field waste under careful operation, members of our organization selected five plots of one acre each as truly representative as possible of the average quality of yellow pine timber. As soon as the timber had been felled the waste between 3 inches and 9 inches was collected, classified and weighed. Much of it was also corded and scaled to determine relations between weight, cord measure and volume. Each stump was measured and its volume and weight computed. Needles from four trees were weighed.

The main points of accumulation of mill waste are the main refuse conveyor and the main dust conveyor. Actual determinations by weight of the amounts of waste carried by these conveyors in very large scale operations were made by members of our staff. The results of these determinations in the field and at the mill enable us to state with a very close approximation to the truth the relative proportions of the initial products of the average yellow pine tree. They have perhaps never been ascertained before within such limits of accuracy or upon so large a scale. The proportions of the several products are as follows:

YIELD FROM ENTIRE TREE.

	Per Cent.
Needles and twigs	2.25
Limbs under 3 in.	2.54
Cordwood	6.42
Pulpwood	4.54
Red and rotten.	6.60
Tops and culls.	22.35
Logs, as indicated	70.56
Stumps	6.48
Lightwood	0.61

YIELD FROM LOGS.
Percentage of Whole Tree.

Red and rotten	1.45
Slabs, edgings and trimmings.....	18.07
Sawdust and shavings.....	17.62
Shingles	0.06
Lath	1.39
Lumber and box shooks.....	31.97
	70.56

Comprehensive studies were conducted on these wastes for a period of eight months. The different classes of wastes were carefully and repeatedly analyzed and their content of rosin and turpentine determined. Papers in great variety were made in our experimental paper mill under direction of V. E. Nunez, and extractions and distillations on the small commercial scale carried out in our Forest Products Department by Dr. L. F. Hawley. The results obtained, together with data from actual commercial practice, point incontestably to the following stupendous totals:

Upon an annual cut of fifteen billion feet of yellow pine the lumber industry in our southern states now wastes raw materials sufficient for the concurrent daily production of 40,000 tons of paper, 3,000 tons of rosin, 300,000 gallons of turpentine, and 600,000 gallons of ethyl alcohol, together with fuel sufficient to meet the requirements of all these industries.

Despite the prevailing opinion to the contrary among lumbermen, and even among paper makers, longleaf yellow pine lends itself admirably to the manufacture of paper. It is too pitchy for the sulphite process but is readily reduced to pulp by the soda process. Much the best results are, however, obtained by the sulphate process, which, when carried out under proper conditions, yields an excellent kraft pulp and paper. The pulp bleaches with some difficulty but may with care be brought to good color without serious impairment of strength. The bleached pulp makes good wood writings and when mixed with pulp from gumwood can be run off into good book papers. A cord and a half of round waste makes a ton of paper as against about two cords of spruce costing northern mills from \$9 to \$13 a cord.

The production of ethyl alcohol from yellow pine waste by the Ewen and Tomlinson process has been fully demonstrated as a technical proposition, about 90,000 gallons of high grade 95 per cent alcohol having been made in the plant of the Standard Alcohol Company, at Fullerton, La. The commercial merit of the proposition remains to be demonstrated since this company is now in the hands of the receiver for reasons altogether apart from the technical merit of the process. It may, however, be said that every technical man familiar with the process believes that it is capable of producing 95 per cent alcohol at a cost, including cooorage and all fixed and manufacturing charges, of not more than 20 cents a gallon. Such alcohol is worth today about 56 cents a gallon. The yield per cord of sawdust or hogged wood waste containing 50 per cent water is ten gallons in large scale

operation, but yields much higher have been obtained in the laboratory.

The process is based, of course, on the observation of Braconnot in 1819 that cellulose, by treatment with mineral acid, is converted into reducing and fermentable sugars. For nearly 100 years experimenters have endeavored to develop this observation into a commercial process. With the exception of Ewen and Tomlinson all have failed to produce alcohol in commercial quantities. Simonsen, in Sweden, in 1889, began a series of brilliant researches which cleared up many points of difficulty and ultimately enabled him to secure very satisfactory results on the large laboratory scale. Attempts at commercial operation, however, developed fresh obstacles and led to the abandonment of the process. The well known German chemist, Alexander Classen, patented during the years 1900, 1902 and 1903 various modifications of the general process of producing sugars and alcohol by treatment of comminuted wood with strong acids under heat. Subsequently several plants were built in this country for carrying out one or another of these modifications. In none of them were any substantial amounts of alcohol produced, and the Classen process must be regarded as commercially inoperative. It remained for Ewen and Tomlinson to overcome the fundamental technical difficulties underlying all these attempts and to put forward the first process capable of large scale production of ethyl alcohol from wood.

The Ewen and Tomlinson process is essentially one for producing fermentable sugars. The fermentation of these sugars, once produced, may be carried out and the alcohol recovered in any distillery by the usual methods. It is my belief that the process affords the cheapest known method for producing these sugars and that it therefore is ultimately destined to become an important, if not the most important, source of industrial alcohol.

In carrying out the process, hogged wood waste, usually containing about 50 per cent of water, is loaded into a rotary digester holding about seven cords and having a protective and heat-insulating lining. Sulphuric acid in relatively small amount is sprayed upon the wood and then steam is admitted to the digester. The critical temperature is reached as quickly as possible and the reaction is then extremely rapid if not indeed nearly instantaneous. Pains are therefore taken to reduce the pressure immediately and to empty the digester of its contents as promptly as may be. About 25 per cent of the weight of the wood is converted to reducing sugars, not all of which are fermentable.

The cooked material, which is not unlike coarse coffee grounds in appearance, is transferred by conveyors to a diffusion battery or other extraction apparatus in which the sugars are dissolved out. The spent chips go to a continuous press for removal of excess water and are then available as fuel. The extracted juice is neutralized with lime and is then ready for fermentation. The concentrated slop from the stills finds use

as cattle feed and is about equivalent to molasses for that purpose.

In a modification patented by me the process may be diverted as a whole to the production of carbohydrate cattle feed. In this modification hydrochloric acid is substituted for sulphuric and subsequently removed so far as is readily possible by heating or blowing air through the mass. The remaining acid is then converted to common salt by the addition of an equivalent amount of sodium carbonate. The juice is extracted and concentrated to the consistence of molasses.

A major economic problem in the South which is bound up with the utilization of wood waste is that of the agricultural development of the cutover lands. It has been demonstrated that by a steam puller yellow pine stumps may be pulled for about 33 cents each. In the trials made the stumps averaged 563 lbs. each, which makes the cost of pulling \$1.16 a ton. Where logging tram roads are still in place, the stumps can be brought to a central plant for treatment at a total cost well within \$2.50 a cord. Treated by solvent extraction they should yield per cord about 6 gallons of turpentine, $2\frac{1}{2}$ gallons of pine oil and 380 lbs. of rosin. The extracted chips, as pointed out by Veitch and Merrill, and amply demonstrated in our experimental paper mill, are available for the manufacture of an excellent grade of kraft paper. Strangely enough, and contrary to our first impression, the charred portions common in such stumps are easily removed in the process and leave the paper clean. The chips are of course also available for alcohol production.

Stumps and the highly resinous wood residues termed lightwood, together with the box slabs from turpented trees, are directly available for treatment by several processes of distillation. The average green wood with 35 per cent moisture contains about 6 per cent rosin, but in selected samples of wood the rosin may run higher than 50 per cent. No large quantities are usually to be had, however, containing more than 30 per cent. The composition of the rosin itself is variable but in green wood it runs about 80 per cent rosin and 20 per cent volatile oils; about 80 per cent of the latter are turpentine and the balance pine oil.

Destructive distillation is carried on in retorts operated commonly without temperature control. Average yields under these conditions are:

Light oils.	Turpentine.	Heavy oil.	Tar.	Charcoal.
6 gallons	6 gallons	16 gallons	48 gallons	35 bushels

Various processes in which the retort temperature is controlled, as in the bath process and the processes of Gautier, Pritchard, and others, have been proposed and several put in operation for a time on either the commercial or large experimental scale. They offer advantages in the way of better yields and quality of turpentine, but these gains are so nearly offset by higher fuel costs and higher maintenance charges that the commercial superiority of these more complicated processes has yet to be demonstrated.

Ten years ago recovery of turpentine from comminuted waste by steam distillation was practised in many plants, the steam being blown through the mass of chips either upward or downward and carrying the volatile oils with it to the condenser. The decline in the price of turpentine in 1907 and 1908 proved so severe a blow to the industry that it is today practically wiped out.

The well known Yaryan process added to the steam distillation method the subsequent step of extracting the chips with a volatile solvent from which the dissolved rosin could later be recovered. Several plants of large capacity were operated successfully until in 1913 the failure of the American Naval Stores Co. caused a heavy drop in the price of rosin which was followed by the failure of the company operating the Yaryan process. A contributory cause may well have been the large losses of solvent incident to the process.

Several methods have been proposed for the recovery of turpentine, pine oil and rosin from yellow pine wastes by the action of water solutions of alkali, but none are thought to be operating commercially. They depend upon the fact that the wood is only slightly attacked by the dilute alkali in which the rosin is readily soluble. Nevertheless, some wood is dissolved and the difficulty of separating this so called "humus" from the rosin has prevented the introduction of processes of this type. The difficulty has been overcome in a simple and ingenious way by Whitaker and Bates, who salt out the rosin soap by increasing, after the initial treatment of the wood, the concentration of the alkaline solution to 3.5 per cent free alkali. The treated chips are then available as a raw material for paper-making.

When the real work of wood waste utilization has once begun and the attention of chemical engineers and financial men has been drawn more generally to the huge potential values now ignorantly thrown away we may expect the rapid development of these byproduct industries and the initiation of many new ones to the great enrichment of the South, and, in somewhat less degree, that of the Northwest. It would doubtless be too sanguine to expect the directive impulse for this new development to come from the lumbermen themselves. They are too close to the wastes. They are blinded by the sawdust. But if they fail much longer to grasp the opportunity which has been so long beside them they must be content to see others reap the benefits and profits which will come through control of processes, special apparatus, and, above all, of technique.

The Brunswick Landeszeitung of January 12, 1916, reports an unusually lively market for potash. The syndicate has orders for 1,500,000 double hundred-weight (220.04 lbs.), which it finds difficult to fill for want of railroad cars.

The CHEMICAL ENGINEER

PUBLISHED MONTHLY by the MYRON C. CLARK
PUBLISHING CO.,

608 S. Dearborn Street, Chicago

*Entered as Second Class Matter, Aug. 19, 1907, at the Post Office
at Chicago, Illinois, under Act of March 3, 1879.*

Subscription—United States, Cuba and Mexico \$2.00
Extra postage to Canada 25c a year; to foreign countries 50c a year.
Remittances may be made by check, draft or money order in favor of
THE CHEMICAL ENGINEER

All communications should be sent to THE CHEMICAL ENGINEER, 608
S. Dearborn Street, Chicago, Ill.

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NOTES AND COMMENTS.

Largest Production of Antimony Ores.

Antimony prices in 1915 were probably the highest known since the metal became a regular article of commerce. The high prices led to the largest production the United States has made and probably the same statement is true for the world's production. According to preliminary figures collected for the United States Geological Survey by Frank L. Hess the production of antimony ores in the United States is estimated to have been about 5,000 tons containing 2,000 tons of antimony, valued at about \$325,000. The largest previous domestic production was in 1892 when 150 tons of metal was produced in San Francisco from Nevada ores and 380 tons of ore carrying 55 per cent of antimony was exported. Practically all operations of the past year were new, most were small, and they were widely scattered so that it is difficult to obtain close figures immediately after the close of the year. Antimony which in July, 1914, had been down to a monthly average price of 7.11 cents for Cooksons, and from 5.44 upwards for other brands, rose gradually though unsteadily, to the end of 1915 when Chinese, Japanese and American antimony were quoted at about 40 cents a pound. Quotations for Cookson's antimony ceased in May, 1915, some time after an embargo had been declared against the shipment of antimony metal or ores from the British possessions, and 50 cents a pound is said to have been paid for it about June 1st, when Chinese was selling for about

35 cents or less. In the fall American antimony appeared on the market for the first time in many years. At first it sold slightly below Chinese and Japanese, but was soon quoted at the same price. Miners and smelters, apparently thinking that the high prices would be temporary, did not begin production as quickly as they otherwise might have done, but before the close of the year properties in Alaska, California, Idaho, Nevada, Oregon, Utah and Washington were producing. Prices for ores ranged from \$1.00 to \$2.10 per unit of antimony. At first only ores carrying 50 per cent or more antimony were in demand, but before the close of the year 20 per cent ores were being shipped from Nevada. From Alaska, according to data collected by Alfred H. Brooks, about 685 tons of stibnite ore carrying 58 per cent antimony was produced in the Fairbanks district from properties on Eva, Vault, Treasure and Chatham creeks. It is reported that 132 tons were shipped from Nome, but it seems probable that more was mined. The largest production was made from deposits near Wild Rose Spring, on the northwest slope of Telescope Peak in the Panamint Range, California. These deposits have been known for many years but have been too far from railroads for profitable exploitation until the past year when prices were high and a branch railroad was built to Trona on Borax Lake, within about 25 miles of them. The deposits contained considerable antimony other as well as stibnite and were mined by the Merchants' Finance Co. (Western Metals Co.). The same company operated deposits 30 miles northeast of Mojave, which are 10 miles from the S. P. R. R. at Neuralia, in Kern County. Other deposits were mined in California at many points in Kern County, in the eastern end of San Bonito County, and on Moore's Flat near Grass Valley. In Nevada considerable quantities were mined at many points mostly in the northwest quarter of the state with Lovelock as a center, but ranging from Pass Canyon in the Pine Forest Range southward to the vicinity of Tonopah and eastward to Joy. Oregon, Washington and Idaho produced small tonnages of ore and in Arkansas a company was organized to work old properties west of Gilham. The Chapman Smelting Co. of San Francisco which had been idle for a number of years again started the smelting of antimony ores. The company mined ore at Bernice, 60 miles east of Fallon, Nevada, and brought ores from other points in the western states, Alaska and British Columbia. The Merchants' Finance Co. built an antimony smelter at Industrial Harbor, Los Angeles. Besides operating California mines the company operated mines in Nevada and bought ores from the western states, Alaska and foreign countries. The Antimony Smelting and Refining Company of Seattle started a plant at Van Asselt the last of the year and made oxide, but metal is to be smelted also. The International Smelting Co. bought ores to be smelted at its South Chicago plant. The Great Western Smelting and Refining Co. of Chi-

ago, and the Pennsylvania Smelting Co. of Pittsburgh have also smelted some ores. The Magnolia Metals Co. found so much difficulty in obtaining needed supplies of antimony at a reasonable price that it bought and mined ores in Nevada, smelting them at Brooklyn. Harshaw, Fuller and Goodwin Co., of Cleveland, were in the market for pure ores from which to make antimony salts, heretofore made from Chinese "crude antimony." The tendency has been for some companies to go to an expense for mine development, machinery and mills, not wholly warranted by the circumstances. The present high prices are necessarily temporary. The Chinese deposits are extensive, and worked by very cheap labor, and other deposits are being developed in other parts of the world, and as soon as the war is over, and possibly before, prices will probably drop to a level with or close to those of 1914.

Natural Gas Production In 1914.

Statistics compiled under the supervision of J. D. Northrop, of the United States Geological Survey, show that the quantity of natural gas commercially utilized in the United States in 1914 exceeded that so utilized in any previous year in the history of the natural gas industry. The quantity produced, which amounted to approximately 591,866,733,000 cubic feet, valued at \$94,115,524, constitutes a new record of production, exceeding by nearly 10 billion cubic feet, or almost 2 per cent, the former record, established in 1913. Increases in output in 1914 over 1913 were credited to New York, Ohio, Oklahoma, Texas, Louisiana-Alabama, Iowa and California, the state last named alone recording a gain of nearly 7 billion cubic feet. Other gas-producing states recorded declines in output, the greatest of which, that of Pennsylvania, amounting to slightly more than 10 billion cubic feet. The increases in gas production may be attributed to various causes—in New York to the increased drilling activity stimulated by the advancing petroleum market in 1913 and the early part of 1914; in Ohio to local extensions of the productive fields of the gas belt in the central part of the state and to the development of an important gas pool in the vicinity of Cleveland, Cuyahoga County; in Oklahoma to the development of gas reserves in the Cushing field, Creek County, and the Healdton field, Carter County, as well as to a decided expansion of the local casinghead gasoline industry; in Texas to a greater utilization of the gas supplies available in the Petrolia and Mexia fields; in Louisiana to the greater development of the gas reserves in Caddo and De Soto parishes; and in California to increased demands for domestic consumption in Los Angeles and adjacent towns in the southern part of the state as well as for industrial consumption in the casinghead gasoline industry. Of the record-breaking production of natural gas credited to 1914 it is estimated that a total of 203,104,358,000

cubic feet, about 34 per cent, was supplied to domestic consumers at an average price of 28.04 cents a thousand cubic feet and that 388,762,375,000 cubic feet, the remaining 66 per cent, was supplied to industrial consumers at an average price of 9.56 cents a thousand cubic feet. During the last four years the ratio of domestic to industrial consumption has varied but slightly. Formerly, however, a relatively greater proportion of the annual yield was supplied to industrial consumers.

Control Food Colors.

A food inspection decision has been issued by the U. S. Department of Agriculture permitting the use of tartrazine in coloring food products. Investigations have shown this color to be harmless and suitable for coloring foods. It is manufactured in large quantities in the United States. Seven other coal-tar dyes have been permitted in foods since the enactment of the Food and Drugs Act. Samples of all dyes certified by the manufacturers are examined in the Bureau of Chemistry and only such dyes permitted as are free from impurities and harmful substances. Another decision has recently been issued making more stringent requirements in reference to the certification of coal-tar dyes when mixed with substances not coal-tar dyes. This decision provides that hereafter the manufacturer shall deposit with the Secretary of Agriculture a declaration that every package in which any such mixture is sold shall have a plain and conspicuous statement of the quantity or proportion of the certified dyes present in the mixture.

Public Hearing Relating to Guaranty Legend on Labels of Foods and Drugs.

A hearing on the question of postponement of the effective date of Food Inspection Decision 153, which in substance forbids the use of guaranty legends and serial numbers on labels of foods and drugs in interstate commerce, will be held in the Bureau of Chemistry, 216 13th street, S. W., Washington, D. C., at 2 p. m., March 10, 1916. This decision, issued May 5, 1914, as originally promulgated, was to take effect May 1, 1915. Later, the date on which it was to take effect was postponed until May 1, 1916, with the proviso as to products packed and labeled prior to May 1, 1916, in accordance with law and with the regulations in effect prior to May 5, 1914, that the effective date was postponed until Nov. 1, 1916. Numerous requests recently have been made to the Department for a further postponement. Those requesting this action represent that manufacturers and dealers still have on hand large quantities of labels printed prior to May 5, 1914, and bearing the guaranty legend and serial number. It is represented that this supply of labels in the aggregate cost many thousands of dollars, and that unless they can be used their owners will sustain a severe loss.

The Chemical Engineer

PUBLISHED MONTHLY

at 608 S. Dearborn Street, Chicago, Illinois

Vol. XXIII.

CHICAGO, MARCH, 1916.

No. 3.

NECESSITY FOR AN AMERICAN DYE-STUFFS INDUSTRY TO AID EXPORT TRADE IN TEXTILES.*

By HENRY HOWARD.†

A year ago, at St. Louis, I discussed the chemical industry under the general subject of "Problems Arising in War and Commerce." At that time importation had fallen off only $3\frac{3}{4}$ per cent from July to November inclusive, as compared with the same period in 1913. Importations of dyestuffs were coming in regularly from Germany and there was no actual shortage. As I pointed out, the greatest effect of the war upon the chemical industry was a national awakening to the absolute dependence of American upon foreign countries for products which are essential to our national welfare.

Germany was strictly limiting us to 75 percent of the tonnage of dyestuffs that we bought from them during the twelve months preceding the war; that is, she allowed us to buy only one-twelfth of this quantity each month, so that, *if we attempted to increase the volume of our textile business and of other businesses using dyes beyond what it was the preceding year, we would be confronted with a shortage of dyes*, and I further pointed out that *this was likely to prove a serious obstacle in the development of any large foreign business in the goods affected*. How true this statement was is now apparent to every one.

Mr. I. F. Stone, president, National Aniline & Chemical Co., recently said:

"I say, therefore, that the German firms are responsible for the difficulty and the acute position of the American consumers. Their primary reason for this holding back of shipments was probably due to the fact that they did not want American consumers to get an oversupply of colors so that they could make up extra quantities of goods which they might use for export to customers in other countries who had formerly bought the same goods from Germany, but who could no longer obtain them."

Within three months after our St. Louis convention,

the importation of all chemical products from Germany was stopped, and we have since been getting along with what had been accumulated outside of Germany plus the amount that our small dyestuffs industry could produce in this country.

There is no doubt that at present Germany has some dyes available for distribution, and the British Order in Council permits its shipment to this country. We must, therefore, draw our own inferences whether Germany does not want us to have these dyes unless we give cotton in exchange or whether she wishes to restrict our activity in foreign trade.

The result has been disastrous to what we all desire—namely: an increase in our foreign trade in textiles. Many textile mills have been obliged to curtail their output at a time when, if we had been independent of other countries, with a dye industry well established, these same mills could have been running night and day manufacturing goods for export and establishing foreign connections by aid of which a considerable percentage of this business might have been retained after the close of the war.

Let us go back for a moment now and see why there is no adequate coal-tar industry in this country. Investigation shows that the fault cannot be charged to the Democratic party but to the strenuous efforts of the foreign manufacturers and American importers, ably assisted by the short-sighted selfishness of these same textile manufacturers who are now the principal sufferers. I believe that, in many cases, these textile manufacturers did not act of their own initiative but were influenced by the clever arguments of American representatives of foreign color manufacturers.

In the winter of 1908-9 I took active part in Washington on behalf of the chemical manufacturers to try and maintain the small protection we had left, and to get suitable protection on basic coal-tar products so that the industry could be established here on a firm foundation from the ground up, because in no other way can it be independent of other nations. Yet our efforts failed, largely as the result of the opposition of the well-protected textile manufacturers.

If you will look on page 146 of the Tariff Hearings before the Committee on Ways and Means of 1908-9, you will find a memorial and protest in opposition to

*Address before the Third National Foreign Trade Convention held at New Orleans, Jan. 27 to 29, 1916.

†Vice-president Merrimac Chemical Co.; Chairman of Executive Committee of the Manufacturing Chemists' Association of the United States.

any advance in duties on coal-tar colors and dyes signed by the following companies:

Amoskeag Manufacturing Co., Manchester, N. H.
 Hamilton Manufacturing Co., Lowell, Mass.
 Pacific Mills, Lawrence, Mass.
 Massachusetts Cotton Mills, Lowell, Mass.
 Merrimac Manufacturing Co., Lowell, Mass.
 Cochebo Manufacturing Co., Dover, N. H.
 American Printing Co., Fall River, Mass.
 The U. S. Finishing Co., New York.
 The Apponaug Co., Apponaug, R. I.
 Gardner & Co., Pleasant Valley, N. Y.
 Passaic Print Works, Passaic, N. J.
 Arnold Print Works, North Adams, Mass.
 Windsor Print Works, North Adams, Mass.
 Renfrew Manufacturing Co., Adams, Mass.
 Queen Dyeing Co., Providence, R. I.
 S. H. Greene & Sons Corp., Riverpoint, R. I.
 Aspinook Co., Jewett City, Conn.

The folly and unreasonableness of the textile manufacturers in lending their powerful influence to the foreign manufacturers of dyestuffs in their successful effort to crush out our coal-tar industry may be appreciated by a consideration of the following figures given by Mr. I. F. Stone in an address before the National Exposition of Chemical Industries, held in New York City last September:

The lines of manufactures which are dependent on their supply of dyestuffs, to continue their regular production, the most important, perhaps, are the textile manufactures, comprising cotton, wool, carpets, knit goods, silk, cordage, shoddy, dyeing and finishing. The following figures are taken from the Census of 1900:

	Establish- ments.	Em- ployes.	Capital.	Salaries and Wages.	Value of Product.
Cotton	1,321	387,771	\$822,237,529	\$147,270,903	\$628,391,813
Wool	985	175,176	430,578,574	82,524,776	435,978,558
Carpets	139	31,706	75,627,010	17,745,092	71,188,152
Knit Goods	371	136,130	163,641,171	52,431,680	200,143,527
Silk	852	105,238	152,158,002	46,097,361	196,911,667
Cordage	164	27,214	76,020,366	10,995,515	61,019,986
Shoddy	88	2,320	6,886,825	1,196,376	7,146,364
Dyeing and Finishing	426	17,303	111,092,654	26,261,431	83,556,432
	5,352	915,858	1,812,212,131	384,522,370	1,684,636,499

When you consider that the value of the coal-tar products annually imported is normally only \$10,000,000, of which not more than 75 percent or \$7,500,000 is used for textiles, an increase of 10 percent in the duty if the whole amount had been paid by the textile manufacturer would have been \$750,000, or less than 4½ cents

$$(\$750,000 \div \$1,684,636,000 = 0.00044)$$

for each \$100 worth of textiles produced, a sum so insignificant that it could have had no appreciable influence on the ability of the textile interests to meet foreign competition, and would have been money well expended, not only as an insurance against the condition which now exists, but would in many cases have resulted in the ultimate lowering of the price of goods in which there is no competition at present.

Few people remember that in 1882 we had quite a flourishing young coal-tar industry which, with consistent protection, would have long since been a large—if not a dominating—factor in our color supply. The fatal tariff reduction was made in 1883 through the initiative of the importers, backed up by the co-

operation of users of colors. Let me quote from a statement made by E. P. Wheeler, Vol. 1, page 230, of Report of the Tariff Commission, 1882:

Would it be a wise policy for us to build up a manufactory of aniline dyes in this country when they can be made more cheaply abroad because the raw material is found in a cheaper condition in England? The English coal, as everybody knows, is richer in the hydrocarbons or inflammable matter than our American coal, and it is well known that we do import to some extent English coal to make gas, although the duty on it is a high one. The only objection that has been or could be made in regard to that would be that if we got into a war with some of the European countries we should be at a disadvantage in regard to these colors. I suggest that that is a very contingent and remote disadvantage; that the possibilities of such a war are insignificant.

In Vol. 1, page 207, there is a letter from H. K. Lansing, treasurer of the Albany Aniline Works, dated Feb. 8, 1882, from which I will quote, and which shows the promising state of the industry at that time:

We are now engaged in the manufacture of all the fine aniline blues, and expecting ere long to make all the finer colors made in Europe. As an illustration of the benefit the country has derived from our efforts, we can state that large crystals of red were sold in 1868 at \$6.50 gold. We now supply the trade with an acknowledged better color at \$2.50 per pound. Blues were sold one year ago at \$4. Since we commenced making, the price has dropped to \$2.50. We think we deserve the sympathy and encouragement of the powers that be.

In refreshing contrast to the textile manufacturers' action in 1908, allow me to quote from a statement of James Hendrick, president of the Albany Aniline & Chemical Works, page 256, Tariff Commission's Report, 1882:

The Pacific Mills and other like manufactories in this country express the strongest hope that we shall receive from you the encouragement we are entitled to. In a letter addressed to me within a week by Mr. Saltonstall, the treasurer, he said there were some importers, or the agents of foreign color companies going through the mills in New England, expecting to get a petition signed in favor of the reduction of the duty on aniline colors, and he said they would have no sympathy from them and cautioned me against them.

The actual disposition of the largest consumers of the anilines is fairly represented by the following sentence in a letter recently received by me from one of these consumers: "The representatives of a large European aniline works are making a great push to have the duties on anilines reduced. I enclose you their circular, which they are sending to all the manufacturers to obtain signatures. What do you as a manufacturer think of it, and what would you propose? We can stand it as it is, and, having all the protection we need on our manufactures, are willing to give all that is required to others."

The subsequent history of the aniline industry is lamentable. The Tariff Act of July 1, 1883, made a heavy reduction in the duty. No new factories were started, and within one year after the new tariff took effect, five of those already established were forced to succumb and go out of business, leaving only four to continue the work. These have since stayed in business, but have not been able to develop to any extent.

In bringing to light past history I do not wish to be understood as bearing grievance against the textile manufacturers for any mistaken policy which they may have heretofore adopted. No one recognizes the

error of this policy more keenly than these manufacturers themselves, and I am credibly informed that they now stand ready to co-operate in any way possible in order to establish a permanent coal-tar industry within the United States.

It is instructive to compare the present condition of textiles in this country with that of iron and steel. The latter industry, thanks to the consistent protection which for years was extended to every branch of the business, is now absolutely independent of the rest of the world in its ability to manufacture all standard grades of iron and steel products in this country, with the result that not only are all American users of iron and steel products getting their supplies as regularly as before the war began, but a large export business is being developed as the result of the paralysis of this industry abroad. In textiles the saving of a possible 4½ cents on \$100 worth of product has resulted in so throttling the textile industry that it is having hard work to supply our local markets, much less to gain a strong foothold in the foreign markets formerly supplied by the belligerent countries.

Now what lesson can we learn from these disquieting facts?

It seems to me that first and foremost it points to the absolute necessity of a permanent non-partisan tariff commission of experts that will sift the facts, analyze the situation and recommend rates consistent with the tariff policy of the party in power, and thus enable Congress to accomplish what it wants to do.

Such a commission should be created at the earliest possible moment by Congress, and if our textile industry is to take any active part in foreign trade during the war the first business the tariff commission should tackle is the study of the chemical schedule with the object of enabling Congress to amend the tariff so as to develop a permanent coal-tar dye industry on a large scale in this country. At present, in spite of high prices, chemical manufacturers have been afraid to invest any large sums in permanent equipment, realizing as they do that as soon as the war is over the industry would quickly disappear under the present inadequate tariff.

Unfair competition is another means by which the foreign syndicates have kept the coal-tar industry from getting a foot-hold here. For instance, aniline oil, one of the primary products, was selling at a high price a number of years ago, and an American company built a plant and started to market its product. Then the price was immediately cut on the imported article to a point about 10 percent below the cost of production in this country, and kept there until the American firm gave up the business. When this result was accomplished, the price was advanced to about the original level.

Again, in 1913, a duty of 10 percent was placed on aniline oil, and the manufacture was again started, with the result that the foreign producers not only absorbed the whole of the duty but actually lowered

the price again to a point where the business showed a loss to the American manufacturer—and this condition was maintained until the war intervened.

Now such competition is manifestly unfair. It is not what might be called legitimate dumping to dispose of surplus product in some foreign country, but is a well-considered policy designed to destroy a new American industry. Such a practice ought not to be permitted, and I think I am right in saying that the present administration has under consideration legislation to prevent it.

There is one other reason—one of public policy—why a coal-tar dye industry is important to the future of this country. At present every one is thinking and talking of preparedness, and one of its most essential items is our ability to produce enormous quantities of high explosives when they are needed. Germany was able to do this over night in the plants used for coal-tar dyes in times of peace. England, France and Russia, substantially without this industry, were almost helpless in this respect, and it may be said justly that the existence of the highly developed dye industry in Germany, coupled with its non-existence in Russia, France and England, has been a determining factor in their relative ability to obtain high explosives, and in the remarkable successes Germany has maintained in the war up to date.

Returning again to textiles. We already produce the cotton for the fabric and all the raw materials necessary for the dyes—how much better it would be for the cotton growers of the South and for manufacturers and laborers of the whole country if *more* finished goods and *less* raw cotton were exported, and the domestic consumption of raw cotton enormously increased.

In closing, I cannot do better than quote from the conclusions in my discussion of this subject a year ago as follows:

Our dependence upon foreign countries for chemicals, whether they be in the nature of raw materials, intermediate products, or finished articles, is a matter of national concern, and I sincerely hope that the Government, the consumer and the chemical manufacturer may unite in friendly co-operation in working toward a common end, viz., the establishment of a coal-tar dye and chemical industry in this country free and independent of all the world.

In all, 3,829,398 lbs. of camphor, valued at \$1,123,630, were invoiced at the American consulate at Taihoku, Taiwan, for the United States during 1915, compared with 3,496,969 lbs., valued at \$1,048,418, for 1914.

The shipments of potash from Brunswick, Germany, for the United States, according to invoices certified at the American consulate at that place, decreased in value from \$4,296,783 for 1914 to \$717,675 for 1915.

THE FOREIGN CREOSOTE OIL SITUATION.*

By G. A. LEMBCKE.

During the months immediately following the outbreak of the European war it looked as if all shipments of creosote oil from Europe were definitely and suddenly stopped. The British, as well as German Governments, immediately placed an embargo on the exportation of creosote oil on the grounds that they needed it for their own purposes.

In Germany, the embargo still exists, in Great Britain it has been withdrawn as the demand of the Government for coal-tar products for manufacturing war material resulted in a heavy accumulation of creosote oil. Confronted with this situation the British Admiralty finally consented to release from time to time, as needed, tank steamers for the purpose of conveying creosote oil to the United States. The shipments of creosote oil from the United Kingdom to this country during 1915 amounted to about 30,000,000 to 35,000,000 U. S. gals. Compared with importations of foreign creosote oils during 1913 of approximately 60,000,000 U. S. gals.; during 1913 of 55,000,000 gals., and during 1914 of 43,000,000 gals., the above importations show a considerable decrease. The year's total imports for 1915 exclude all German and Belgian oils, and consisted of British creosote oil only.

Due to the fact that several of the large railroad systems, on account of uncertainty of supplies, decided to abstain for the time being from the use of creosote oil, as well as to the depressed general conditions in this country, particularly during the early part of 1915, the importations during 1915 sufficed to meet, in a measure, the somewhat decreased demand.

How the position is going to shape itself during 1916, or even beyond that, is largely dependent on the duration of the war. If the war should be protracted for another year German and Belgian supplies will not be available for importation. This loss, however, will in all probability be slightly offset by an increased quantity of creosote oil available for shipment in the United Kingdom, where as a result of the increased demand for coal-tar products a good many by-product ovens have replaced the old bee-hive ovens.

Prices for foreign creosote oil in this country will remain about on the present level as long as conditions are as just outlined. Even should the war end some time during 1916 it is not reasonable to suppose that a decided change in price will take place.

Stocks in Germany are entirely exhausted, and exports after the war must of necessity at first at least be slow and reduced in volume. In Great Britain and the other countries involved in this war an immense amount of renewal work must be done after peace

is declared, and, therefore, European consumption will be increased while the total output of creosote oil probably will assume ante bellum proportions.

THE ROLE OF THE CHEMIST IN THE CEMENT INDUSTRY.*

By C. N. WILEY.

Much mystery attended the processes employed in the early manufacture of Portland cement. When the brick layer of Leeds discovered that he could make an artificial water cement from a mixture of Thames chalk and Medway mud, he took every precaution to insure that none should discover the secret of his process. When engaged in making his raw mixture, it is said that he attired himself in flowing black gown and the pointed hat of a mystic and performed curious incantations over his operations. I. C. Johnson in 1845 wrote: "Thus he had a kind of tray with several compartments and in these he had powdered sulphate of copper, powdered limestone and several other matters. When a layer of washed and dried slurry and the coke had been put into the kiln, he would go in and scatter some handfuls of these powders from time to time as the loading proceeded, so the whole thing was surrounded by mystery."

One can imagine with what intense interest Mr. Johnson observed this remarkable procedure and it is small wonder that he was fired with a stronger determination to know of what the composition of this cement consisted. Procuring a sample, he had one of the most prominent chemists of England make an analysis and the chemist's report that the substance contained 90 percent phosphate of lime mystified Johnson still further. But thinking that at last he had won the secret of this hydraulic compound, he made a large collection of bones from the butchers of the city and proceeded to calcine them. Needless to say, he was induced to discontinue his operations by the outraged citizens of the vicinity.

So up to this time, the chemist proved rather an obstruction than a help to the solution of the cement problem. But by the world-old method of trial and error, Johnson at last succeeded in making a cement which was equal in every respect to that of Aspdin and from this on the industry began to expand and thrive.

In the early days of the Portland cement industry, the correct adjustment of the proportion of carbonate of lime to clay was purely an empirical process. In the first place, mixtures were made in varying proportions from which samples of cement were prepared and the proportion giving the best cement was adopted. Any irregularity due to variations in the chemical composition of the materials, or carelessness on the part of the workmen, was ascertained by sampling the mixture frequently, the samples being

*From a paper presented at the 12th Annual Meeting of the American Wood-Preservers' Association, Chicago, Jan. 18-20.

*Address presented December, 1915, before the Alabama Section of the American Chemical Society.

burned in a trial kiln. From a close observation of the resulting cement, when tested for soundness, color, etc., the "sampler" was, by long experience, enabled to judge whether the correct proportions were being maintained. This was a tedious and an unsatisfactory process, for while a sample was being prepared and tested, the bulk it represented had passed beyond the reach of alteration. If the slurry was run into backs, any error was corrected by altering the mixture and luting or stirring the contents of the back, from which a sample was occasionally prepared. With the Goreham process, no alteration of the previously prepared mixture was possible; it would probably be dry and ready for the kiln before the results of the sample were known. If the contents of any particular drying-flat or chamber proved to be over- or under-clayed, the burner could be instructed to burn it lightly or heavily as the case might be and this was really all that could be done.

When it is remembered that if the materials are in the first place suitable, success depended on the proper proportion of the carbonate of lime to clay and that for the same material this proportion was a constant one, it is evident that, if the carbonate of lime in a normal sample was known, the correctness of the mixture could be checked by the determination of this substance in the trial sample. And it was upon this determination that chemists depended largely for the proper composition of their mixtures.

An instrument known as Scheibler's calcimeter, originally devised by Dr. Scheibler for determining the amount of carbonate of lime present in animal charcoal used in sugar refining, was frequently employed for determining carbonate of lime in Portland cement mixtures. The principle of its action is well known to chemists and it was the principal instrument of mixture control in the cement industry up to ten years ago. The results obtained through it, although "near enough" for many technical purposes, were far from accurate. The carbonic oxide evolved is collected over water in which it is to some extent soluble and a correction has to be made dependent, of course, upon the volume of gas evolved. The Lunge nitrometer, in which the gas is collected over mercury, was also commonly used. Very little knowledge of chemistry or chemical manipulation was necessary for the use of the calcimeter or nitrometer.

Thus in the early days, the chemist was hardly known in the cement industry and it was unthought of for a cement manufacturer to employ the exclusive services of a professional chemist. The employee responsible for the maintenance of a correct and uniform mixture of raw materials was but a workman of more than the ordinary intelligence whose success depended on the rapidity with which he could make his test burnings and the degree of memory he possessed in profiting by past experiences.

Redgrave remarks in his book on calcareous cements that "the sample kiln should not be ignored

when working with new and untried materials and much may be learned from the methods of the old-time sampler, his methods of work and the unconscious instinctive way in which he reasoned from the appearance of his samples. It should not be forgotten that Portland cement was discovered by a bricklayer and that its reputation was established long before the process of manufacture became a scientific question."

In this country, the early manufacture of Portland cement was chiefly confined to the Lehigh Valley region through which ran a belt of argillaceous limestone, the composition of which was almost in the exact proportions for making a high-grade cement equal in every respect to the more complicated mixtures of European manufacturers. The process of trial and error was largely responsible for the early success of men like D. O. Saylor and it was not until somewhat later that the chemist was first called into consultation and his advice was asked more for the purpose of locating new deposits of suitable rock and in the working out of problems which arose in the operation of the manufacturing process.

John W. Eckert may be called the father of cement chemists in this country. At the time Saylor and his associates were perfecting their processes above Allentown, Eckert was working as an assistant to Professor W. H. Chandler at Lehigh College, now University, South Bethlehem, Pa. He was asked to make analyses of rock from the different beds in the quarries of the Coplay Cement Works, of which D. O. Saylor was president. Cement was then made from each of these distinctive rocks and these cements were analyzed. In this way it was determined which beds were suitable for Portland cement and the other beds could be used in the manufacture of their Anchor brand natural cement. In his report of 1875-6, the state geologist commenting on this says that "much technical and scientific supervision is necessary to determine which stone to use and which to reject in order to make a cement capable of undergoing the tests now applied by engineers and architects." So it might be said that the activity of the chemist in the cement industry depended greatly on the increasing severity of the specification laid down by engineers and architects.

Eckert was finally engaged by the Coplay Cement Works to devote his entire time and knowledge to the process of manufacture and he thus became the first cement chemist in this country. His efforts resulted in more certainty and less chance in the preparation of proper mixtures and a more uniform product naturally resulted.

Somewhat later, Robert W. Lesley, one of the pioneer manufacturers, was experimenting with the bricks into which the slurry was pressed preparatory to burning and he solicited the co-operation of George W. deSmedt, then a Government chemist engaged in the study of asphalts and kindred materials.

Together these two men worked out various problems and were the first to mix the slurry with hydrocarbons before casting into bricks. The incorporation of this hydrocarbon not only made an excellent binder but in the kiln the burning out of this binder rendered the brick more or less porous so that the mass could be more evenly burned.

Lesley and deSmedt also discovered the difference between crystalline and gelatinous silica and Lesley took out a patent for the manufacture of gelatinous silica which they thought was of great importance.

All cements in those days were quick-setting and many efforts were made to retard this setting for obvious reasons. When P. I. Giron, affectionately called "Pig Iron" by his men, a French chemist in the employ of the Atlas Cement Co., was in France he had noticed the workmen adding a white substance to cement before they applied same in building sidewalks. As gypsum was in common use in France in building operations, he suspected that this was the white material and he found that by adding a small amount of this substance to the cement, the setting time would be materially lengthened. Dyckerhoff in Germany was also making use of plaster to season his cement and he obtained a slower setting cement. Lesley took out a patent for seasoning cement, the principle of which was to sprinkle the clinker with sulphuric acid.

The question as to what Portland cement really is early received much attention from investigators. Chemical investigations, so far, have failed more or less completely to throw light on the complex structure of this substance, although mineralogical examinations have been more successful. Although chemical methods have failed to reveal the actual structure of Portland cement, much has been learned by the study of synthetic compounds. Probably Vicat was the pioneer in this line of research, followed by Rivot, Chatoney and Fremy.

In Germany, Heldt, Fuchs, Schott, Michaelis, Erdmenger, Dyckerhoff, Meyer and others were attacking the problem along this line. Up to 1885 the various theories advanced defined more or less definitely the chemical composition of the cement, but all believed that upon addition of water the cement broke down into simpler compounds and free calcium hydrate. Believing that if this free lime could be removed from the anhydrous cement much more could be learned of the actual composition, investigators sought reagents by which this extraction could be accomplished. Rebuffat was the first to make use of an aqueous sugar solution, but Michaelis and Feret objected that results obtained in this way must be incorrect.

Probably the most satisfactory test which we have for free lime is that devised by Professor A. D. White. The method is based on the formation on the slide of a microscope of a characteristic crystalline calcium phenolate readily recognizable in polarized

light. The reagent is prepared by dissolving crystallized phenol in an immiscible and rather non-volatile solvent, such as nitrobenzol, and adding a trace of water. Thus it is possible, by this test, to determine whether the chemical balance between the calcium and the other constituents in a good cement has been attained.

As mentioned above, much has been learned of the constitution of cement through mineralogical investigations. As these investigations were conducted in many cases by chemists, it is only proper to grant the chemist credit for his part in solving the problem. LeChatelier was one of the first to attack the problem along these lines and he was followed by many investigators. In this country, the work was being carried on by such chemists as Richardson, the Newberrys, Campbell and others and much was learned from their experiments. Several years ago, Day and Sheperd and scientists of the geophysical laboratory have, from extensive investigations, come to a conclusion as to the true constitution of Portland cement and they are now engaged on studies of hydration.

The technical chemist has not had the time to devote nor the opportunity to pursue investigations like the above but he has contributed to the knowledge of the subject in no small degree by working out technical processes whereby a high-grade product may be made and maintained. He has found that the cement rocks of the Lehigh Valley are not necessary for the production of a high-grade product but has gone into almost every state of our Union and has found there materials which when properly combined would produce a Portland cement of high quality. On account of the variation in composition of these raw materials, he has developed methods for their proper control. The increasing severity of cement specifications has caused a greater watchfulness throughout the process of manufacture until at the present day the chemist has in control every step of the process from the time the rock is won from the deposit until the finished cement is placed in the hands of the ultimate user. And he has gone yet further, for he has shown the user how this cement may be used to best advantage and has pointed out the necessity for closer inspection of the materials with which it is combined.

The chemist has shown that a true Portland cement can be made from blast furnace slag, heretofore a waste product. The utilization of this waste product has resulted in a great industry producing over 10 percent of the total production in this country.

So in these years of progress and expansion, the cement industry has seen the humble "sampler" develop into the present highly trained scientist whose word is law concerning the process of manufacture. The chemist alone is responsible for the quality of the product, and the fact that American-made Portland cement is recognized as superior to that made in other countries is a tribute to the untiring efforts and ability of our chemists.

THE TURPENTINE INDUSTRY IN THE SOUTHERN STATES.*

By CHARLES H. HERTY†, Ph.D.

A railway trip through the coastal plain of the South Atlantic and Gulf States, from North Carolina to Texas, shows on every side fallen and charred remnants of trees, stumps innumerable, and occasional huge piles of sawdust. It is a desolate scene in those sections where agriculture has not yet been developed. It represents the destructive path of the naval-stores industry, followed more or less closely by that of lumbering, through that rich, natural heritage of long-leaf pine forests which originally covered completely this entire portion of the country.

From these forests the world has received its chief supply of spirits of turpentine and rosin, averaging in value in recent years some forty or fifty million dollars annually. Yet in the production of this great crop only a very few have received for their toil more than a bare livelihood. The great mass of the turpentine operators have toiled throughout the years in rugged earnestness, in robust health from the out-of-door life in the pine forests,—but always on the outer edge of developing civilization, with few of the comforts and conveniences of life, indifferent to the utter lack of efficient business methods in their operations, and strongly wedded to woods practices which have been handed down from generation to generation as they steadily moved from North Carolina toward Texas.

If the traveler, however, should leave the main lines of travel in Florida or the more westerly states, and by tram or team reach some of the more remote sections, he would find beautiful virgin forests of this same long-leaf pine, the rich brown trunks of the trees, free from low-lying limbs, bearing aloft rich crowns of green, and firmly rooted below in a soft carpet of the same hue, formed by the "wire grass" which abounds throughout this territory.

Will the operator, in the exploitation of these remaining forests, profit by the demonstrated inefficiency of past methods? Can he change his attitude of thought toward the living tree on which his operations are based? Is he willing to place himself in line with all other lines of modern industrial life, which have realized, or are beginning to realize, that true progress in any industry must be based, not upon individual opinion or hereditary teachings, but upon scientific research and constant striving for greater efficiency?

Upon the answer to these questions depends largely the future of the naval-stores industry. This is not a matter for indefinite proceeding along inefficient lines; the actual life of the industry is threatened, for the once-considered inexhaustible forests are rapidly dis-

appearing. At the present rate of destruction the end can be fairly well forecasted, especially since no effort is being made toward reforestation.

It was natural that destructive methods should have characterized this industry, for the early settlers in eastern North Carolina found forests of long-leaf pine everywhere. Clearance was necessary for agriculture, crops had to be grown, lumber was needed for industry, homes had to be built, and so the work of destruction began.

It was immediately recognized that this tree, when wounded, is a prolific producer of an oleoresin, "crude turpentine." Furthermore, the rich resinous wood, when heated out of contact with air by piling in heaps and covering with earth, gave off a rich distillate of tar, which could be boiled down to a pitch. These products, tar and pitch, were much needed for the wooden ships with their extensive rigging, at that time universally in use; and so along with agriculture, with its yearly crops, there developed the naval-stores industry with its constant output of immediately marketable products.

The method of conducting the industry called for no plant other than the forests, and so when the yield of the trees began to decrease after two years of operation, new tracts were opened, and the industry began its march southward, from North Carolina into South Carolina, thence into Georgia and Florida, and then rapidly expanding into the Gulf States, though on a smaller scale.

In the early days in North Carolina no effort was made to separate the crude turpentine by distillation into its constituents, spirits of turpentine and rosin, the gum being shipped to northern cities or to England for such manufacture. In the early part of the past century, however, this manufacture was transferred to the woods, iron stills being at first employed, which later were replaced by the more efficient copper stills such as are used today for this purpose.

In the woods, however, there was no corresponding advance in methods of operation, with the exception of slight improvement in the tools employed. Thus for more than a hundred years the method of wounding the tree and collecting the gum remained the same throughout the turpentine belt.

The normal routine on all turpentine farms consisted of the following operations:

"Boxing.—In the winter negro laborers, under the direction of a white woodsman, cut 'boxes.' The box was an elliptical cavity cut in the base of the tree, usually just above the junction of a prominent root with the trunk of the tree. It served to collect the gum which flowed during the warmer months from the scarified surface above. The tool used in cutting this box was a very long, narrow axe, the negroes developing consummate skill in the use of this 'box axe.' The standard dimensions of the box were 14 ins. width, 7 ins. depth, and 3½ ins. from the outer wood toward the center of the tree. The number of boxes

*From a paper presented Nov. 4, 1915, at a joint meeting of the Section of Physics and Chemistry of the Institute and the Philadelphia Section, American Chemical Society.
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per tree was increased from one to four, and occasionally five, according to increasing diameter of the trees.

"Cornering."—Box cutting was followed by "cornering." This consisted of removing two triangular chips from immediately above the box by means of the usual wood-chopping axe. The function of cornering was to provide smooth surfaces to direct the flow of the gum into the box.

"Chipping."—As vegetation became active in early spring the work of scarification of the trunk of the tree began, and continued weekly for eight months. The repetition of this process was necessary, as the flow of gum, greatest during the first three days following the fresh chipping, practically ceased after one week. The tool employed in chipping, called a "hack," was a stout U-shaped steel blade attached by a metal shank to one end of a round wooden handle. This handle carried on its other end a heavy iron weight which gave momentum to the free arm stroke used to draw the blade through the bark and outer sapwood. A slightly modified form of this tool, called the "puller," was mounted on a much larger handle, with no iron weight attached, and was used for the higher reaches of the third and fourth year of scarification.

"Dipping."—At periods of four to five weeks, when, in the judgment of the woodsman, the boxes showed an average filling, the gum was removed into buckets by a broad, flat, spear-shaped tool, called a "dip spoon." Barrels placed at convenient distances in the woods received the gum from the buckets, and were then hauled to the "still" for distillation.

"Scraping."—As the chipping season progressed not all of the gum found its way to the box, for as crystallization of the gum began some of this mass remained sticking to the exposed surface of the tree. At the close of the chipping season this accumulated resinous mass was scraped from the trees, giving thus the name, "scrape," to the product. Its content of spirits of turpentine was much lower than that of the gum from the boxes.

"Raking."—With the completion of the scraping, the final operation was the protection of the trees from the ground fires which prevail throughout the turpentine belt in late winter when the dead wire grass is burned. Such protection, "raking," was effected by means of a common hoe, all combustible material, chips, pine needles, and dead grass, being removed to a distance of about two feet from the base of the tree.

This completed the year's operations in the woods, and the cycle was then renewed from year to year.

The severe strictures on the wastefulness of the industry spoken of by the German technologist, Otto N. Witt, led to the determination on the part of the writer to investigate whether or no this criticism was deserved. Correspondence with men familiar with the industry, and a brief visit to a turpentine farm in South Georgia, afforded ample proof that conditions were even worse than had been depicted.

With such waste prevalent, could not something be done to improve the situation? Here the methods of work learned through research in a chemical laboratory asserted themselves. A search of the literature was begun and made as comprehensive as possible. The result of this study and of observations in the woods made clear the fact that the great evil of this industry, that which more than all else was responsible for the waste and destruction, was the cutting of the "box" in the base of the tree. This deep cavity, located just where the strain was greatest, caused many of the trees to fall in even slight windstorms. It constituted a great source of danger during fires, especially after turpentine operations had ceased and the tree no longer was protected by the annual "raking." The decreased vitality of the tree, due to the severe wound, led in many cases to easy attack by injurious insects. Such evils were easily noticeable, but others, less readily seen, were found upon closer study. With a receptacle at a fixed point, while the distance between the receptacle and the freshly-chipped surface increased regularly from week to week, opportunity was thus afforded for increasing loss of the volatile oil by evaporation, for coloration of the resin by absorption of oxygen from the air under the influence of sunlight, and for waste in dripping outside the box. It seemed reasonable, moreover, that this severe wound would so decrease the vitality of the tree as to cripple, at least to some extent, the power of the tree to produce crude turpentine. The "box," therefore, should be the primary point of attack in any effort to conserve these forests.

To overcome the evils of the "box," a substitute receptacle must be provided which should inflict but a slight wound in placement on the tree; should be capable of removal at convenient intervals to a point just below the chipping surface; should be extremely simple in its construction, in view of the gummy character of the product it was to receive; easy of operation, because of the unskilled labor which would use it; and cheap, if hopes were to be entertained of its commercial introduction by those who were abundantly satisfied with existing methods and fully convinced that no better could be found—an unfortunate state of mind in these days of progress.

The literature of the French system of turpentine was then studied, and the records of the Patent Office were thoroughly searched. Nothing, however, was found quite free from objections to its ability to meet the above requirements, especially as applied to the system of chipping as practiced in the Southern states. In the light gained from this study, however, a substitute was devised, consisting of a simple cup suspended, through a hole near its rim, on a common nail. Into this cup the gum was to be directed by two shallow galvanized iron troughs or gutters, to be inserted about one-quarter inch deep by one of their long edges in correspondingly shallow inclined cuts across the scarified surface of the tree.

With this apparatus provided, and again following the procedure of laboratory research, preliminary experiments were begun, during the summer vacation of 1901, in the forests of southeast Georgia, near the town of Statesboro, on timber provided, after much persuasion, by some of the leaders of the industry in Savannah, Georgia, who viewed their concessions with an eye of infinite skepticism.

The results of these preliminary experiments were the thorough demonstration of the efficiency of the apparatus, a deeper grasp of the problem to be solved, a genuine sympathetic interest with the personalities of many employed in the industry, and much knowledge of the habits of the pine. It was completely demonstrated that the dark color of rosin produced under the box system, after the first year of operation, was not at all due to physiological changes in the pine, but solely to the method of collecting the gum. Under this system opportunity was offered for increased oxidation and for absorption of the deeply-colored gum coating the exposed surface, formed by the chipping of previous years. This latter point was important, as the commercial value of the rosin decreases as the depth of color increases.

The United States Bureau of Forestry, hearing of the proposed preliminary experiments, tendered the writer a collaboratorship in order to secure publication of the results. The experiments were so full of promise that it was agreed that the work should be promptly resumed at the opening of the next season, with field experiments on a commercial scale, under the auspices of the Bureau of Forestry. Accordingly the experiments were begun in February, 1902, on the turpentine farm of Powell, Bullard & Co., a well known firm operating in southeast Georgia, near the town of Ocilla.

For these experiments the following policy was adopted at the outset:

First, the timber was to be provided by the firm; the cups and gutters and cost of installation, by the Bureau.

Second, the labor was to be none other than such as was employed in the regular work of the farm.

Third, the experiments were to be restricted solely to the "box" question and the practicability of the substitute cup and gutters. Therefore the work of chipping, dipping, and scraping should be conducted in the normal way.

Fourth, four sets of comparative experiments were to be conducted simultaneously, one on virgin timber, and three on boxed timber which had already been operated respectively one, two, and three years. This would determine, so far as possible in one year, the influence of the box on the timber and on the income of the operator.

Fifth, the results should be taken from the records of the company, whose statements would be readily accepted by all other operators.

So far, so good. Then troubles began. The manufacturer, delayed in his work, did not deliver the equipment until the chipping season was nearly at hand. This led to shortcomings, undreamed of at the time, and which in after years caused the loss of many thousands of dollars; but this will be discussed later. Next, labor troubles were unexpectedly encountered. The negro laborer proved even more conservative than the white operator and woodsman, and assumed the remarkable attitude that the "flower-pot" method of making turpentine was more properly the work of women and children, and not suited to the dignity of full-grown men. This may be difficult of belief, and it was strange in the light of later developments, but it proved a serious obstacle for some time. By dint of patience, tact, and kindly reasoning this trouble was at last overcome sufficiently to enable a beginning of work in the woods with three laborers, but up to the very moment of actual handling of the axe the chagrin and mortification of those three negroes, too inefficient for the regular box-cutting squad, were comical, though the situation had its serious side in that the whole question of the carrying out of the experiments was at stake in the successful solution of this labor difficulty. It is sufficient here to state that in a short while the problem was completely solved, and as success in the experiments became more and more marked the comical picture then became the rather haughty air and proud demeanor of those who gleefully dubbed themselves "cup niggers!"

To return to the experiments: three crops were selected, consisting each of 10,000 boxes, the unit of operation. These three had already been under operation one, two, and three years respectively. On one-half of each of these crops cups and gutters were installed near the point where the chipping would begin. On the other half the gum was collected in the normal way, in the box, at the base of the tree. These experiments would determine the practicability of the equipment at varying heights on the tree; the quality, as to color, of the rosin produced from gum collected under the two systems; and would give some information as to relative waste from evaporation, etc.

The main interest, however, centered in the experiment on virgin timber, where the two systems could be put into operation under fully equal conditions. For this experiment a tract of timber of fair average quality was selected by the firm just outside of the town. To insure accuracy of the experiment, this timber was carefully and repeatedly cruised by experienced woodsmen, and a division made as to location of cups and boxes respectively. In this division it was decided to alternate the "drifts" (subdivisions of a crop) of cups and of boxes. This also furnished more uniform weather conditions in working the two halves. The entire crop was to be chipped by one man, and the dipping was to proceed every three weeks simultaneously in the cupped and boxed halves of the crop, the gum to be collected in different sets of barrels. The

presence of varying amounts of trash and water would render inaccurate the results from measuring or weighing the gum. Therefore it was distilled and record kept of the number of gallons of spirits of turpentine obtained from each lot, and separate sales made of the rosin produced. No difference in quality of rosin was expected or found here. As the distance of flow of the gum was the same in each set, loss of spirits of turpentine by evaporation was equalized. All precautions were taken so that whatever difference of results might be found in the yields, from the two halves could be ascribed to no other factor than the influence of the severe wound caused by box cutting on the productive power of the trees. The advancement of the idea that it decreased productive capacity had met with hoots and jeers on all sides; and here in this crop, it was felt and stated without the least effort of repression, would be demonstrated the superiority of the judgment of the "practical" man over the theoretical college professor.

The work of installation began. Two flat faces meeting in a central line were cut with common axes to adapt the round tree to the straight-edged gutters, two laborers with broadaxes made across these plane surfaces the incisions for the gutters, which were promptly inserted by another group of laborers, the upper gutter reaching just to the center of the face and emptying into the opposite gutter equally inclined, running about one inch lower and extending about two inches beyond the angular center of the face, to provide a suitable hanging of the cup into which all of the gum dripped. While awaiting the arrival of the cups and gutters, the box-cutting squad and the "cornerers" had been gleefully at work in the other half of the crop.

With the respective receptacles provided and installed, the work of chipping began—and the race was on. The detailed results are given in Table I.¹

TABLE I.—FIRST-YEAR CROP—DIPPINGS.

Number of dipping.	Date of dipping.	Number of chip-pings.	Barrels of dip obtained.		Spirits of turpentine on distillation (gallons).		Excess spirits of turpentine (gallons).	
			Boxes.	Cups.	Boxes.	Cups.	Boxes.	Cups.
1....	April 14.....	3	*9¾	†7¾	101.6	81.3	17.3	
2....	May 5.....	3	9¼	10½	111.0	130.5		19.5
3....	May 26.....	3	12	14½	136.8	178.3		41.5
4....	June 16.....	3	12¾	17¾	143.3	191.2		47.9
5....	July 7.....	3	12¼	14¾	142.4	175.2		32.8
6....	July 28.....	3	10½	12¾	115.2	141.7		26.5
7....	August 18.....	3	10	11¾	106.6	126.6		20.0
8....	September 8.....	3	8	10¼	86.1	105.9		19.8
9....	September 29.....	3	7¾	9¾	80.8	106.0		25.2
10....	November 4.....	5	†10¼	12¾	110.9	145.6		34.7
Total			32	101½	1,134.7	1,385.3	17.3	267.9

* Including resin from box cutting and cornering.

† Including resin from placing cups on trees.

‡ Boxes dipped after trees have been scraped.

¹The tables throughout this paper are from Bulletins 40 and 90 and Circular 34 of the United States Forest Service.

The unexpected shortage from the cups on the first dipping led to great rejoicing among the box supporters, and to undoubted apprehension on the part of the solitary backer of the cups. The second dipping, however, altered the situation, and by the last of June the victory for the cups was so complete that all were converted. The beginning of the end of the box system had been reached. From this point on all went well. Labor was anxious to enlist, enthusiasm had supplanted scoffing, and now the chief effort of the original cup backer was to guard against possible inflated results, due to some over-zealous convert, which results might not be justified by the facts in the case, for in spite of convictions formed in advance of experiment it was, as in all research, the truth which was sought.

Several years passed, much thought was expended, and many experiments were made before the true in-

TABLE II.—SEASON'S RECORD OF NET ROSIN SALES.

Half crop.	From dip.	From scrape.	Total.	Excess net sales.	Per cent excess net sales, cupped trees.
First year:					
Cups	\$101.72	\$47.72	\$149.44	\$ 85.51	23.50
Boxes	328.40	35.53	363.93		
Second year:					
Cups	266.34	49.25	315.59	144.13	81.64
Boxes	104.51	66.95	171.46		
Third year:					
Cups	171.27	27.41	198.71	132.65	200.80
Boxes	39.49	26.57	66.06		
Fourth year:					
Cups	167.33	29.23	196.56	132.56	207.13
Boxes	36.09	27.91	64.00		

terpretation of that shortage on the first dipping was obtained and its remedy provided. This will be discussed later.

Meanwhile the distillation of the gum from the second, third and fourth year crops showed uniformly high-grade rosin from the cups, as contrasted with the low-grade rosin from the corresponding boxes, and the equipment proved itself readily adaptable to the increasing heights of chipping.

The results of net rosin sales from all four crops are given in Table II.

The experiments with the second, third and fourth year crops were discontinued at the end of the year, having served their purpose. The working of the virgin crop, however, was continued two years longer. The complete results for the three years' operation of this crop are given in Tables III, IV and V.

That the distribution of the timber in this virgin crop had been well equalized was shown by measurements of diameters of all trees in the crop and by a determination of the average number of cups or boxes per tree throughout the crop.

As the work progressed, careful record of the dead and down trees were made in each half. The count at the end of the three-year period is shown in Table VI.

During the chipping season portions of some of the

chipped surfaces became unproductive, locally termed "dry face." The results of the measurement of the extent of "dry face" in the two halves of the crop showed an excessive amount in the boxed half at the end of the first year. From that time on the amounts, while increasing in each, showed less striking difference. Evidently the cause of increased "dry face" in the last two years lay more and more in the chipping, and this observation led to later valuable experiments on comparative yields from lighter chipping.

The results of the first year's experiments were communicated to the turpentine operators at their annual convention. Much interest was aroused and some enthusiasm. The next few months, however, proved an interesting testimonial to the "follow-up" policy of the wise advertiser, for, in the three-month period spent in arranging for the manufacture of the equipment at a reasonable cost and in the preparation of an account of the experiments for publication as a government bulletin, interest in the matter completely disappeared. It was only through the most persistent efforts that interest was sufficiently re-aroused, in those at one time enthusiastic, to assure the commercial utilization of the rather limited output of the cup system.

This first season's use of cups by the operators assured the future, the results obtained more than confirming the experimental results of the previous year. Instantly the demand increased; prejudice slowly gave

way; the quality of the cups was improved with increasing experience at the factory; timber owners made concessions on price of leases, provided cups instead of boxes, eventually stipulating that timber could not be worked if box cutting was the intention; and labor throughout the territory became familiar with and enthusiastic about the new method. Thus was the box system, with its attendant losses, replaced by the more efficient cup system. Today box cutting is practically a thing of the past, while many forms of cups, to suit individual requirements, have become everyday articles of commerce.

TABLE VI.—RECORD OF DOWN AND OF DEAD TREES.

	Number of trees blown down.		Number of trees dead.	
	Boxed.	Cupped.	Boxed.	Cupped.
In 1 year.....	8	3	35	16
In 2 years.....	60	34	139	83
In 3 years.....	78	44	217	150

From the outset, railway officials of the Southern states, keenly alive to the welfare of the territory tributary to their lines, were strongly sympathetic with this movement, and by their prompt and intelligent handling of the question of freight rates on the equipment facilitated greatly the universal introduction of the new method.

To encourage the adoption of the new system, the Forest Service adopted the wise policy of offering, free of cost to the operators, the services of the writer

TABLE III.—SPIRITS OF TURPENTINE FROM HALF CROPS.

Year.	Cups.						Boxes.			Excess from cupped half crop.	Net price per gallon at time of operation.	Value of cup excess.
	From dip.			Total.	From dip.			Total.				
	Gallons.	From scrape.	Gallons.		Gallons.	From scrape.	Gallons.					
First	1,383.3	205.0	1,590.3	1,134.7	153.7	1,288.4	301.9	40	\$120.76			
Second	1,103.5	165.0	1,268.5	705.2	226.6	931.8	336.7	45	151.52			
Third	781.3	136.0	917.3	536.1	190.5	726.6	190.7	45	85.82			
Total	3,270.1	506.0	3,776.1	2,376.0	570.8	2,946.8	829.3	..	\$358.10			

TABLE IV.—NET SALES OF ROSIN FROM HALF CROPS.

Year.	Cups.			Boxes.			Excess from cupped half crop.
	From dip.	From scrape.	Total.	From dip.	From scrape.	Total.	
First	\$401.72	\$47.72	\$449.44	\$328.40	\$35.53	\$363.93	\$85.51
Second	286.88	58.24	345.12	132.42	84.08	216.50	128.62
Third	212.60	61.65	274.25	124.76	79.70	204.46	69.79
Total	\$901.20	\$167.61	\$1,068.81	\$585.58	\$199.31	\$784.89	\$283.92

TABLE V.—SUMMARY OF GAIN FROM CUPPED HALF CROPS.

Year.	Spirits of turpentine.			Rosin.	Total.
	From dip.	From scrape.	Total.		
First	\$120.76	\$85.51	\$206.27		
Second	151.52	128.62	280.14		
Third	85.82	69.79	155.61		
Total	\$358.10	\$283.92	\$642.02		

TOTAL VALUE OF PRODUCTS FROM THREE YEARS OF OPERATION.

Cupped half crop	\$2,688.55
Boxed half crop	2,046.53

Gain from cupped half crop \$ 642.02 = \$1,284.04 per crop.

in inaugurating the work on a turpentine farm. Never to be forgotten was the first experience in this work of instruction, when on a cold, drizzly February day, at a South Georgia saw-mill, there was handed over for instruction a group of sixteen young negro convicts, in characteristic garb and utterly devoid of any knowledge of turpentine operations. The situation seemed impossible and hopeless, but the future of the work was at stake. Fortunately experience gained in years of teaching in the class-room came to aid. The setting was entirely changed, but the methods of pedagogy were applicable and necessary. The effort succeeded. After such an experience all others were easy.

"The practical man," however, had his inning, for a little later, working in timber near the Gulf Coast of Florida, it was found that such timber was so tough that it was impossible to make smooth, flat faces on

the tree for the gutters with the ordinary axe employed. After a long day of struggle, with defeat clearly ahead, the turpentine operator suggested the use of the broadaxe for this purpose. The experiment was tried and immediately succeeded. Later another step forward was taken by the suggestion of another operator that in hewing with the broadaxe the beveled side of the edge be placed next to the tree. This was revolutionary from an axeman's point of view, but it was tried and its advantages were immediately noted, for there was no difficulty in forcing the axe to the surface at the base of the cut, thus saving the tree much useless wounding and so increasing the speed of operations that in a little while it was possible, with an equal force of laborers, to install three crops of cups while one crop of boxes was being cut. Such details may appear trivial, yet each had its influence on the rapid introduction of the system.

As reports began to arrive concerning commercial experiences with the system all agreed on increased yield, but all agreed likewise on the unusually large number of chippings required to fill the cups with gum at the beginning of the season, especially when compared with boxes on similar timber near the cupped trees, the capacity of cup and box being the same. After this first dipping the superiority of the cup system readily showed itself in largely-increased yields. Here was a recurrence of the mortifying experience with the first dipping of the virgin crop in the experiment at Oeilla. What could be its explanation? How could the trouble be overcome? Various suggestions were made and numerous experiments tried by men of all types in all sections, but without success in overcoming this chief defect in the system.

A few years later the writer had opportunity to visit Professor A. Tschirch in his laboratory at Berne, Switzerland, and there learned his views concerning resin flow, views based on the results of experiments on many pines in the neighborhood. According to Tschirch the resin ducts, found scattered throughout the wood of a normal pine, contain a resin which is formed as a result of natural life processes in the living tree. Such a product is, therefore, a purely physiological product, and such ducts he designated "primary resin ducts." These yield only a small quantity of crude turpentine when the tree is wounded. Immediately after the wounding, however, there begins in the outer fresh wood the formation of a very large number of resin ducts, both above and below the wound, forming an anastomotic system, which pour out crude turpentine in great quantity as a healing balsam over the wound. Such an exudate is a pathological product, and the ducts producing it he termed "secondary resin ducts." These extend four to five inches above the wound, requiring four to five weeks for their full development.

In the light of this knowledge the explanation of the excess yield of the boxes over the cups on the first dipping was simple. When the boxes were cor-

nered a full-width, V-shaped surface was formed above which the secondary resin ducts formed in abundance during the several weeks which elapsed before the chipping season began. Then when the first chipping was made the cut, traversed secondary resin ducts along its full length and a maximum yield was obtained. On the other hand, the late arrival of the cups for the experimental work made it necessary to begin chipping immediately afterward. The secondary resin ducts had not fully formed during this brief interval, and there was a correspondingly low yield of crude turpentine, which, however, rapidly increased later as the ducts increased. Again, in explanation of the same difficulty experienced by operators who placed their cups on the trees many weeks in advance of the chipping season, it must be remembered that the flat faces for the gutters were then being made on the tree by the broadaxe. The cutting of a straight-edged tool into a round tree exposed the fresh wood above in the form of two curved lines, meeting at the center of the cut surface. Again, the secondary resin ducts formed, but following the outline of the cut. When, therefore, these trees were chipped only about half of these ducts, those near the center, were traversed by the downwardly-inclined stroke of the hack. Hence a flow of gum far below that in the box system, but again rapidly increasing after the first full-width cut formed by the first chipping. This suggested a simple method for overcoming the losses encountered during the first six or eight weeks of operating under the cup system; namely, the placing of the gutters on the trees in winter should be followed immediately by one full-width chipping and the trees allowed to stand, without further chipping, four or five weeks. Opportunity would thus be given for full formation of the secondary resin ducts along the full width of the chipping surface, as in the box system.

These views were laid before a number of operators using the cup system, and they were requested to try the modified method on some of their timber during the next winter. They agreed: the experiments were carried out, and in every case the cure for the evil was found to be complete, cups so placed yielding a greater amount on the first dipping than boxes or than cups placed without the one winter chipping. Conservative estimates made by experienced operators place the total annual gain from this slight modification of woods practice at not less than \$500,000. Could there be asked a better illustration of the value of pure university research, as was that of Tschirch, for efficient industrial operation?

With the future of the cup system assured, attention was next turned to the relative yield of crude turpentine with reduced wounding of the tree in chipping. These experiments were conducted near Green Cove Springs, Florida.

In order to interpret the results clearly, all trees were cupped, and one of the crops chipped to normal depth, seven-tenths of an inch into the new wood, the

thickness of the chip being such as to carry the chipping up the trunk at the normal rate. This crop was designated A.

In another crop, designated B, the depth of the chipping was reduced from seven-tenths to four-tenths of an inch, all other conditions being identical with the standard crop, A.

In a third crop, designated C, the thickness of the chip was so reduced that the same elevation on the trunk would be reached in four years as was reached in three years in crop A, all other conditions being alike in the two crops.

Finally, in a fourth crop, designated D, no tree under ten inches was worked; the minimum diameter for trees bearing two cups was raised from twelve inches, as in crop A, to sixteen inches; and, finally, no tree bore more than two cups, regardless of its larger diameter. In this crop the chipping was the same as in the standard crop, A.

The results of the four years of work on these crops are given in Table VII.

TABLE VII.

Crop.	Dip.		Scrape.	
	Yield.	Increase.	Yield.	Increase.
	Pounds.	Per cent.	Pounds.	Per cent.
A	206,235		17,742	
B	211,911	2.75	44,838	
C	214,503	4.01	39,775	
D	279,260	35.41	53,915	12.93

The marked success of these experiments led to a further experiment for one year, in which was compared with a standard crop, such as A above, the yield from two crops, designated G and H, in which both modifications of chipping, shallow and thinner cuts, as in B and C above, were combined. The results are given in Table VIII.

TABLE VIII.

		TABLE VIII.			
Crop.		Number Yield of			
		Number	of chip-	dip.	Increase.
		of cups.	pings.	Pounds.	Per cent.
Walkill	Turpentine Company	9,880	35	90,094	..
G		9,880	35	124,292	38
H		9,880	35	121,474	35

Thus was the way clearly pointed out for more conservative treatment of the trees, the result being largely-increased yields.

Are further experiments on the reduction of the wound in chipping justified? This is a difficult question to attempt to answer. Certainly there is a limit to which such reductions can be carried, beyond which financial loss will result, under existing conditions of cost of stumpage and wages of labor. If the tree is not wounded, crude turpentine is not produced; if it is girdled, the tree dies. Somewhere between these extremes lies the most efficient operation. From the results already mentioned it is evident that past practice in chipping has been on the side of too excessive wounding. Whether or not the limit should be further reduced can be determined only by experiment.

One abuse, however, has arisen in connection with the spread of the cup system; namely, the general practice of cupping very small trees. Such trees were not

brought into operation under the box system, as they were too small to receive a box, but they could be cupped with ease. Two strong objections hold against this practice. *First*, the trees of the future naval-stores industry are being destroyed, a well-marked case of child-labor abuse for which there is no legislative correction. *Second*, the judgments of the leaders of the industry agree that the operation of such small trees is unremunerative in itself, yet often producing sufficient crude turpentine to seriously depreciate the market value of that produced from the larger trees. Much has been spoken and written by these leaders against the practice, but still it continues. Is not experiment advisable here? The following is suggested, and it is hoped that the suggestion will receive the consideration of the United States Forest Service. An investigation is needed of what is the actual yield from a crop of ten thousand of these very small trees during a period of three or, better, four years of operation. Such an investigation would give facts where now mere opinion prevails. The experiment would not be costly, because it could be carried out in connection with the regular operations of a turpentine farm. It would require only efficient supervision; the dipping from the small trees to be kept separate from those of unquestioned size, say ten inches and over in diameter; the yields from the two lots compared, and the results published for the benefit of all. Such a publication would constitute a valuable contribution to the literature of this subject, and such facts would carry far more weight than any amount of spoken or published criticism.

Leaving now questions connected with woods-practice, let us follow the barrels of gum to the distillery, or "still," as it is uniformly called. This manufacturing plant is exceedingly simple, and, as a rule, roughly built, the rapidly-shifting character of the industry not justifying more pretentious housing. A large copper kettle, the "still" proper, is set in brick masonry above a fire-box in which wood is burned. Eight to ten barrels of the gum, mixed with chips, dirt, and some water, constitute a charge, the distillation of which requires from three to four hours. The kettle is connected by a removable "still head" to a coiled copper worm, set within a large wooden tank, the condenser, into which cold water flows or is pumped at the bottom, cooling thus the hot mixed vapors of steam and spirits of turpentine in the condenser coil. The heated water is led off by an overflow or is partly used by running along a narrow trough leading from the top of the condenser to a small, funnel-shaped opening in the lower part of the still head, and emptying into the still and on to the boiling gum below, the steam thus generated aiding materially the separation of the volatile spirits of turpentine from the non-volatile rosin. The proper regulation of this flow of water has been generally determined by the sound produced by the boiling mass heard at the mouth of the condenser. Recently the use of inset thermometers for the pur-

pose of controlling the distillation has largely increased. The condensed liquids, flowing from the mouth of the worm, separate at once in the receiving vessel into two layers. The lighter spirits of turpentine is pumped into large storage tanks or is dipped into oak barrels, which have been thoroughly coated inside with glue. It is now ready for marketing. When the volatile oil is practically all removed, the still head is taken off, and the chips are skimmed. In the case of virgin dip this skimming is done as soon as the gum melts and before distillation begins. Finally, when all water has boiled off, a necessary precaution to prevent the rosin being opaque, the molten rosin is allowed to flow from the still through a tail pipe, leading from the bottom of the still, to two strainers placed the one above the other. The upper strainer consists of coarse wire gauze, and retains unskimmed chips. The lower strainer, of fine brass gauze over which are placed layers of cotton batting, retains the dirt and smaller portions of trash. From these strainers the rosin flows into a long wooden vat, from which it is promptly dipped into barrels, where, upon cooling, it solidifies and is then ready for shipment.

Crude as the method appears to the casual observer, nevertheless careful study of this system as compared with the much more expensive systems in France has convinced the writer that, given a good stiller, equally good results are obtained by this very inexpensive outfit. Of course, the presence of the personal element, as represented by the stiller, is always a risk in manufacturing operations, and it would seem to be a needless risk in the light of its complete elimination in the French system of "mixed injection," where heating is effected partly by free flame and partly by steam; where water vapor is furnished both by inflowing hot water and by direct injection of steam; and where operations are controlled entirely by the thermometer. Such plants are not expensive and are very simple in operation.

The suggestion has recently been made that this industry would be placed on a much more efficient basis if the smaller stills in the woods were done away with, the gum hauled in tank cars direct to a central distillery, advantageously located, and there distilled. This suggestion contains many thoughts which justify the belief that here lies the way to the next decided step forward in the evolution of this industry, if questions connected with transportation can be properly worked out. Undoubtedly there is much waste at the present small distilleries. Important matters concerning utilization of by-products cannot be properly handled under the present system. Much demoralization of labor arises from the still being near the turpentine camp. On the other hand, the handling of crude turpentine in sufficient quantities at a central distillery would justify the presence of the most efficient forms of stills and of labor-saving devices common to all handling of material in large quantities. Of possibly still greater importance is the fact that operations on such a scale

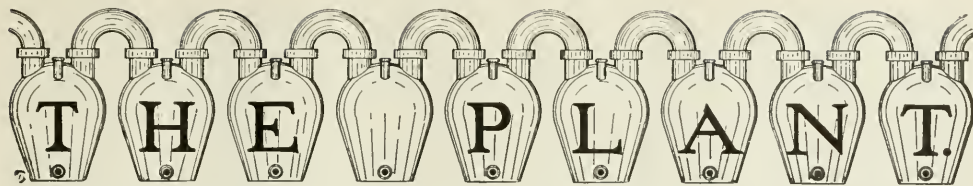
would justify the employment of competent chemists, who, in addition to the careful control of the operation of the distillery, could supervise the manufacture of rosin oil directly from the molten rosin, of the various commercial articles into which such products enter, and who could by systematic research find new uses for and new transformations of the various products, thus guiding the industry to wider fields of application, and enabling it to more fully keep abreast of that progress characteristic of all industries which wisely make use of the services of well-trained chemists.

Dr. Henry K. Benson, professor of industrial chemistry at the University of Washington, in Seattle, has been appointed director of the newly established Bureau of Industrial Research, the first such institution on the Pacific Coast. One fellowship dealing with a problem of the iron and steel industry and amounting to \$2,000 has already been established as a result of the co-operative spirit existing between the Bureau and the business men of the Pacific Northwest. Other fellowships are contemplated. Men interested in the by-products of the fisheries industries have also assigned one of their problems to the Bureau for special investigation. The Bureau will attempt to co-ordinate the research activities already undertaken by the university, with a view to the utilization of the resources of Washington.

According to a circular issued by the Russian Minister of Finance and received from the office of the Russian commercial attaché in New York, the date for closing the international competition for inventions by which alcohol may be utilized for industrial purposes has been changed from January 1, 1916, to September 1, 1916, and the date for awarding the prizes is postponed to March 1, 1917. The Russian international competition for the discovery of substances best suited for denaturing alcohol is also open until September 1, 1916. The prizes for this competition, according to Handelsberichten, The Hague, are 30,000, 15,000 and 5,000 rubles (\$15,450, \$7,725, and \$2,575 at the normal exchange rate of \$0.515 to the ruble).

A process for making an artificial silk that is claimed to more nearly approach pure silk in luster than any now on the market has been invented by a Japanese, who uses chrysalis oil and mulberry cellulose dissolved in a proper solvent. The fiber is produced in the customary way for forcing the liquid through minute holes.

Ferromanganese amounting to 14,838 tons, valued at \$1,029,727, was invoiced at the American consular agency at West Hartlepool, England, for the United States during 1915, compared with 27,229 tons, valued at \$1,471,017, for 1914.



SULPHITE COOKING WITH FORCED CIRCULATION.*

By EINAR MORTERUD.†

The dissolving of intercellular substances in plants, as known, is brought about partly by alkaline and partly by acid liquids. Both of these processes have to be carried on at an increased temperature; consequently heat must be supplied. Cellulose was produced from straw by an alkali process, this being the first application of chemistry to pulp manufacture. After that came wood, also dissolved by alkali, and some time later came the acid process, first used by the brothers Tilghmann in Philadelphia. But the Tilghmanns gave up the experiment and, as is known, the Swede Ekman is considered to be the first who produced sulphite pulp as an article of manufacture; this was in October, 1874. About the same time, Professor Mitscherlich, in Germany, appeared with his method for the sulphite process.

All cellulose manufacture up to that date was based on indirect heating. The Ritter-Kellner process from Austria was the first process in which direct heating was used. About that time, both Mr. Flodquist and Mr. Francke in Sweden presented rotary boilers and direct steam, but it may be remembered that Mr. Flodquist made his first boiler for indirect heating with coils of pipe. This did not hold, the pipes fell down during a boiling and the boiling had to be continued with direct heating, giving the best of results, and so his process became a direct process.

The fact that in the beginning both procedures of producing cellulose from vegetable matter provided indirect heating for the alkaline process, was caused by the high price of the chemicals used, their recovery being of vital importance; with the acid process the difficulty lay in producing a liquor of the required strength.

For the alkaline process it was evident that the recovery of the chemicals would be absolutely necessary in order to get a sufficiently low producing cost, and as the recovery method consisted of evaporating the lye, indirect boiling was always used and this was done by direct heat under the boiler or by steam heating.

Indirect heating was necessary for a long time in the acid process, for the reason that the boiling liquid could be made economically by a weak solution, and a

further dilution with water, which would follow a direct influx of steam, was also prevented.

Later on these conditions became of less importance owing to the fact that for the alkali process the cheap acid sodium sulphate began to be employed, instead of expensive sodium oxide; it therefore became practicable to use direct steam and pay for the evaporation of the lye.

In the sulphite process such a mastery of the acids was attained that even in summer it was possible to make a strong acid.

While economy in chemicals was making necessary these restrictions in the heating process another demand had to be observed, which was to get the best possible production, first of all getting a uniform production at one boiling point which would not give a quality of the first, second or third grade. This drawback was especially noticeable with the Mitscherlich boiler, but it was also evident in vertical boilers directly heated. Such unevenness in product was caused, of course, by the absence of uniform conditions in boiling, and as only two agents are influential in causing the dissolution of intercellular matter, setting the cellulose free, these being the chemical composition of the boiling liquid and the temperature, it was endeavored to remedy the defect by giving the whole boiler a rotary motion in order to effect a mixing.

It is a difficult problem to rotate an indirectly heated boiler. It has been tried with vertical rotating (Mr. Ekman's boiler was a vertical rotating cylinder boiler), as well as with horizontal rotating, but anyone will understand that working with such pressures and such a temperature as is the case with the alkaline process, this idea of rotating cannot be considered a good technical solution of the mixing problem. There is always something uncanny about these vertical revolving boilers and even the most ardent admirers of them never attempted to work with one of larger capacity than about 1,059 cubic feet.

All that is now left of rotating cellulose boilers is the little vertical sulphate boiler. The fact that for the alkaline process the rotatory form is kept, is accounted for by the necessity of looking out all the time for the recovery of the chemicals, to which end the entire boiling is blown over into a diffusor, leaving the whole mass of fibers in a condition that permits of practical washing.

Conditions are quite different as regards the acid process where there never was any idea of utilizing the black lye. Here, a bottom part suitable for blowing off the production never had to be taken into con-

*From Paper. An address before the Norwegian Technical Society of the Paper Industry. Translation from *Papir-Journalen* for the News-Print Manufacturers' Association.

†Tønderød, near Moss, Norway.

sideration; accordingly, for sulphite boiling the horizontal rotating boiler and its construction went far ahead in dimensions. It has been said that sulphite digestors have been built up to a capacity of 5,297 cubic feet, but when of this size, they seem to get rather heavy.

The aim has always been to obtain an even boiling. It has been endeavored to obtain uniformity of temperature by means of injectors, especially in the alkaline process; but in such cases direct steam is necessary and this, of course, is not a convenient way of heating if the black lye has to be concentrated. To keep up so sensitive an appliance as an injector and at the same time attain a circulation that proves really efficient is not possible, which explains why none of such construction may any longer be found.

Experiments with a view of obtaining circulation by means of different temperatures have not been successful; it is plain that with such an arrangement the result will be just the opposite from that hoped for. Only with a forced circulation by mechanical appliances and with a heating apparatus outside the boiler can uniformity of cooking be obtained.

THE BOILER.

It is unquestionable that developments point to bigger and still bigger dimensions of boilers. This is plainly indicated in the sulphite process where boilers of a capacity of 10,594 cubic feet are now a reality.

To heat indirectly a boiler of 7,062 to 10,594 cubic feet by tubes inside the boiler would be a slow process and any larger amount could not be obtained thereby. To heat partly indirect, which is done everywhere with vertical boilers (pretending to boil indirectly), will be only a half measure, and I want to say on the spot that when I talk of indirect heating I mean the real thing, that is, all the heat within the boiler, practically speaking, without so much as a drop of water added to the boiling lye.

If a real indirect heating of the big boiler is to be effected it is impossible to do it by any other means than by a calorifier. By the term calorifier I mean an appliance located outside which heats and boils the acid liquid indirectly by a steady circulation. It will be practical to use it with the largest boilers which can in this manner be kept free from all rigging with pipes and pipe holders, leaving them unencumbered so that the boilers can be built in place for a convenience of filling and emptying. Without question it is the vertical shape which is to be preferred and which already has taken the lead. But, in my opinion, the shape of the bottom ought to be changed. A screen or sieve must be placed there for the purpose of holding the wood during the circulation of the lye. This sieve must be placed so as not to be in the way of discharging the digester, and the emptying must be made central, preferably by blowing. This is meant for sulphite, as for sulphate it is already an established rule to blow the cook.

The reason why I think that blowing has to be used again is that through the use of the circulating calorifier in boiling and with the acid strength completely governed, there can no longer be any unboiled parts which in the blowing would make impure, discolored pulp.

Using tubes inside the boiler for heating leads to many and great inconveniences. The tubes become leaky, the condenser being thereby rendered useless. The tubes require room; they break or bend in the wall on the holders; they are difficult to insert and take out, and by loosening and falling out of packing the pulp is impaired in quality. Last, but not least, they have a very poor effect, in reality only about one-sixth to one-eighth the effect per square foot of the heating surface of a calorifier.

An apparatus outside the boiler can be so constructed that all these inconveniences may be omitted. The pipes will be free to expansion caused by differences of temperature, thereby eliminating at once all danger of leakage, while the condensing water will prove an absolutely reliable feeding water. The pipes must be so made as to be easily taken out and put back. It will be a practicable operation to change pipes while the boiling is going on. Deposits on the heating surfaces cannot be mixed up with the pulp, and such deposits, by a special arrangement, can be taken care of. All this is possible only when the apparatus is placed outside the boiler.

The heating surface can be made as large as desired, either by big single appliances or collectively by batteries of two or more units.

By arranging the heating surface in the center of several boilers, it is plain how much more economical such an arrangement is than if heaters are placed inside each boiler, even presuming that the heater in each instance would be equally effective, which, however, they would not be.

It must be remembered that as soon as the boiler has been brought to the right temperature, the heater has no longer anything to do in the boiler. Not only is it lying there useless, but it is exposed to the danger of corroding. Therefore it will have to be admitted that that system is the right one which is so arranged that one organ of the system having acted its part, it can be removed or uncoupled, so as not to be a hindrance or be exposed to damage, and when the same organ can be made to serve the same purpose in another system.

The circulation apparatus must be mechanical and not based on temperature. Therefore hardly anything else than a pump can come under consideration and the choice will fall on a centrifugal pump. I have been here considering only the sulphite process and will continue on that subject. For sulphate boiling the problem is easier though it also has its specific requirements.

A centrifugal pump which must work in warm sulphite lye is really something terrible to think about

and I have been very modest in my claims. But results have surpassed all my best expectations and such a pump has now been working for years at a minimum cost of maintenance.

The last apparatus in the system is the condensing pump, which carries the condensing water created in the calorifier back to the steam boiler. Plainly, a better feeding water could not be had than chemically pure distilled water, but it is to be observed that it is pure only when the apparatus does not leak, and this one does not leak, in spite of everything.

This condensing water will change its temperature with conditions, as in the beginning of the boiling, when the digesting liquor is cold, the water will cool down also. On account of these conditions the pump has to work under many different pressures. But the greatest difficulty was experienced in the fact that the water to be pumped often reaches a temperature up to a manometer pressure, which comes very near the boiling point. The shape in which these pumps are now made have, however, proved that such difficulties can be eliminated by having been in use for years.

In practical sulphite work the boiler must be fully filled with acid as in complete indirect heating, as no liquid at all must enter the boiler after the cover is screwed on. During the operation of filling the digester the top valve in the circulation system must be kept closed.

The circulation is then to be started and steam started in the calorifier, at the same time the valve leading the condensed water to the condensing pump must be opened. It must be apparent that the immediate steam consumption, or, in other words, the immediate heating, depends on the quickness with which the condensing water formed can be removed from the calorifier. Thermometers are attached to the in and out going circulation pipes, making it possible to note the highest as well as the lowest temperature which may exist in the boiler at any time.

Supposing the boiler to be well filled as described, it is carried as quickly as possible up to 314° to 315° F. As is well known, there cannot be any dissolving of incrustations below this temperature, and it would therefore be only a waste of time to use a long heating period. Consequently any shortening of this dead period is equal to a gain in production.

After this temperature has been reached with the boiler entirely filled, the temperature is increased more and more, according to the quality of pulp which is to be produced. It will never be necessary to interrupt the heating in consideration of the gassing processes. There is no necessity for any standstill as the idea of any such stops simply was to give the boiler time during after-circulation to equalize the differences in temperature which must occur in the direct steam boiling.

On account of the even temperature and the lively circulation the pulp will be boiled to the quality desired with less use of heat. When the boiling has

reached a certain point, the great amount of liquid is no longer required. This quantity of liquid is only to be used for a thorough soaking of the pulp; as soon as this purpose has been attained, or, in other words, when the danger of getting scorched wood splits (so called "coffee beans") is passed then this big quantity of liquid has no longer any mission. It is then to be removed by leading it directly into a boiler made ready to start. In that way is obtained:

1. The saving of the heat required to bring this amount of liquid up to the highest temperature.
2. A great part of the required total heat is carried over to the new boiler without cost. Or, in other words, a certain quantity of liquid almost at its highest temperature is transported from one boiler to another.
3. A still more concentrated black liquor, which is of the greatest importance at a later period of recovering.

The foregoing steps insure a better utilization of the chemicals in the digesting liquor, as the transporting of liquor to the next boiler enables us to reuse them.

This calorifier heating with forced circulation simplifies the whole boiling process, and it is under better control. The two thermometers, one on the inflow, the other on the outflow, will give a reliable average temperature, whereas the single thermometer used on ordinary boilers gives only a local temperature. The same can be said of the lye test. It is plain that with a vigorous circulation the test will be a sure average proof. In short, boiling with forced circulation can never surprise us with a "throwing" (settling) of the acid. This even distribution of temperature and of lye strength will act as intended on the quality and on the quantity of the production. The increase of pulp through these uniform dissolving conditions may be estimated at from 4 to 6 percent.

In sulphate work the boiler is to be filled with the same amount of lye as customary, with the addition of so much swell lye as corresponds to the increase of boiling liquid caused by condensation of steam from direct boiling. For this boiling a high temperature has to be attained at once, while the customary outlet of the gas is at the same time effected.

The rotating boilers ("steep boilers") now reigning supreme in the sulphate industry are going to be supplanted in the same manner as the rotating boilers in the sulphite industry. In this case even much larger dimensions for boilers will be possible and sulphate boilers of from 3,531 to 4,238 cubic feet capacity will be the smallest. However, this change will not be brought about all at once, for the reason that the volume of the boiler determines at the same time the diffusing volume. If the boiler dimensions are changed there must also be a change in diffusers. I am of the opinion that developments will go along the lines of washing out in the boiler. At any rate, I will not go into this any further now. I am going to switch over to the results achieved up to the present.

In Moss' cellulose mill, where the first one of these boilers was put in operation on October 15, 1913, that is more than two years ago, the apparatus has not required any repairs as yet. Renewal orders for four boilers, which were started six months ago, now show the following results:

The production has increased by 40 percent as twenty boilings a day are now made against sixteen formerly.

The consumption of coal and the heating surface of the steam boilers, despite the increased production, are the same as before, constituting therefore a saving of 40 percent.

But in the soda house, where the black lye is evaporated, things are going on still more lively. Formerly four ovens were used with a great extra consumption of coal and wood for the evaporating. But now with an increase in production of 40 percent only three ovens are in use and all coal and wood consumption has stopped. Not only that, but there is even more heat than needed, so that more water than before has to be drawn from the diffusers.

Of course, a new steam boiler will now be installed to utilize surplus heat and I have little doubt that in this boiling method it will be possible, without any pipe evaporator, to obtain a boiling of the pulp not requiring the use of coal or any other fuel but only the heat from the incrustations.

As far as the pulp is concerned, the production is considerably more even and larger. The consumption of chemicals has been reduced by about 10 percent. The total saving in this boiling process, at prices now quoted for coal and other material, I may estimate at about \$3.65 to \$3.89 per ton of pulp. This in itself is a very respectable saving but I permit myself to call further attention to an increase in production of 40 percent, which alone should prove the value of the process.

Regarding the cost of maintenance it may be said that the apparatus running the longest, that is two years, has caused an expense of \$8.04 for repairs.

In the sulphite mills the savings effected are not so great, inasmuch as the concentrated lye is of little importance, but the day may not be so far off when the black liquor in the sulphite mills will be an article of great importance, and recovery processes will be devised, more effective than those used in the sulphate process.

In the Waldhof sulphite cellulose mill in Germany an apparatus was put on trial three months ago, and in Zsolna, the largest sulphite mill in Austria, an apparatus was started six months ago.

In Waldhof, for instance, it has been found through the most minute investigation, by bleaching proofs, by microscope and by stretching proofs of finished paper, that we produce ever a better pulp in shorter boiling time and the reduction in boiling time is from three to five hours in every boiling.

DEVELOPMENT IN THE UNITED STATES OF THE MANUFACTURE OF PRODUCTS DERIVED FROM COAL.*

By H. W. JORDON.

During 1915 we read statements in the press, almost daily, giving the impression that the American chemical industry was wholly unable to manufacture synthetic coal products, and that the only relief in sight was from the wonderful discoveries of a small group of chemical amateurs who, having patriotically hurled themselves into the situation since the war began, were on the verge of evolving the entire 900 synthetic coal-tar dyes and the whole list of pharmaceuticals, from palmetto and other sources hitherto unsuspected as being fundamental to organic chemical products. These statements, by implication and by omitting mention of the extensive plants put into operation by established chemical companies in 1915, tended to create the public belief that these companies were doing nothing to supply the American market.

Some of the most important products which were widely heralded as having been produced for the first time in America in 1915, were manufactured by these companies 15 to 30 years ago. Benzol and its homologues have been regular American products, with shipments in carload lots or tank cars, and with occasional exportation to Europe since 1900. Salicylic acid was manufactured at Jersey City by Zinsser & Co. from 1880 to 1897, when foreign competition closed the plant.

Synthetic carbolic acid was manufactured by the Semet-Solvay Company from benzol at Syracuse in 1900 and the following years, in quantities up to 2,500 pounds daily. This carbolic acid was synthesized into trinitrophenol, commonly known as picric acid, which was bought by the United States Government for use in national defense.

The United States had several well-equipped plants, prior to 1885, for manufacturing the principal coal dyes of that day. The industry grew, and produced an increasing number of synthetics, from which all those survive which could surmount the natural and artificial barriers in the road to a complete American coal products industry. The best of these manufacturers have continued without interruption, and constitute the main body of our present organic chemical industry.

The failure of the daily press to give credit for the large amount of capital invested, and for the extensive work accomplished during the past year, is not fair to these American companies that built up our great chemical industry during the past thirty years, and who are now the prime movers in expanding our American coal products industry to meet the new conditions.

*From a paper presented before the American Institute of Chemical Engineers.

The Benzol Products Company is an example of this growth. Organized in 1910 by men long associated with the acid, alkali and coal products industry, it began the manufacture of aniline salt at Frankford, Pa., in the plant operated several years ago by the late Dr. Jayne. Although the company's output of aniline in 1910 was but a small percentage of the American consumption, the English and German producers immediately dropped the price from 10 cents or 11 cents per pound, where they had held it for several years, to 9 cents or 8 cents per pound. Most American consumers refused to buy this American aniline at the fair price of 9 cents to 10 cents at which it was offered, and followed their usual custom by supporting the cut-rate foreign producers.

These American consumers were the very ones who rushed to Washington when the war began, and frantically implored the Department of the Interior to dig up right away, quick, some unfailing source of supply to provide the 2,000 or more synthetic coal-tar dyes and pharmaceuticals that had required forty-five years of German science and organization to develop. The trip to Washington was easy for them. They had been there repeatedly since 1880, whenever a tariff bill was under consideration, to advocate no tariff on dyes.

The Benzol Products Company did receive the support of a few far-sighted American consumers, who realized that the permanent establishment of aniline manufacture in the United States was of far greater value than the saving for a few years of 2 cents per pound. With their support the manufacture of American aniline was continued. A new plant has been built at Marcus Hook, Pa., put into operation in August, 1915, with ultimate capacity equal to the former total United States consumption of aniline. Notwithstanding war conditions multiplied the price of its raw materials, benzol, sulphuric acid and nitric acid, the company sold its aniline at a price less than half the prevailing market price of aniline for 1915. This production of aniline, supplemented by that of a few other plants, has supplied the American market to a fairly comfortable extent.

The Benzol Products Company's aniline has been distributed, by preference, to those consumers who employ directly or indirectly the greatest number of people. The important fact is that in 1916 a supply of aniline equal to the former American consumption will be available at fair prices, and that this supply is not coming from mysterious or untried sources.

Since 1900 the production of benzol in the United States has steadily increased so that there was enough benzol at all times for the manufacture of dyes, if the industry had been established by the assistance of the Federal Government and by the sustained support of the American textile manufacturers. Not only were both these lacking, but the textile manufacturers persistently favored the English and German producers in preference to any American manufacturers.

Benzol supply is only one factor, and alone it is not sufficient to justify the very heavy investments required to establish an American coal products industry. In 1915, several steel companies operating by-product coke ovens, installed benzol recovery plants, so that a heavy production of American benzol is assured. When the war ends the output from these plants will be so abundant that it may become available as motor fuel for automobiles. In this service 1 gallon of motor benzol gives 15% greater mileage than a gallon of gasoline.

Under the abnormal conditions and inflated prices caused by the war, many small plants have sprung up and produced products derived from coal at a profit. At the end of the war these plants will fall like autumn leaves. A few may struggle on and consume their war profits in an endeavor to establish permanent business, but only those built on a firm economic basis will survive.

The manufacture of products derived from coal is not an industry by itself. It is founded upon, and is an extension of, the manufacture of mineral acids and alkalies, and was created as a means of making a wider market for those acids—sulphuric, nitric, hydrochloric, acetic, for chlorine and the like, and a market for the alkali products, soda ash and caustic soda. For this reason a permanent coal products chemical industry cannot be created in America except by co-operation with, or extension of, the American acid and alkali manufacturing companies.

In 1915, with prices ten to fifteen times normal, it was possible to manufacture some coal products with large profit in the United States. With the return to normal conditions we must conduct our processes with keenest attention to the most scientific methods, because losses of 1 or 2 percent in the steps of manufacture means bankruptcy.

Proof that Americans sadly lack this scientific detail was given in 1915 by the many serious accidents, fires and explosions in plants manufacturing these products, the cause of which was faulty engineering design, inexperienced superintendence, untidy plant housekeeping and careless workmen. With unconscious humor, we have done homage to German efficiency by ascribing these accidents to the German diplomatic service.

To illustrate the necessity of attention to detail, take the synthetic manufacture of carboic acid. This process, starting from pure benzol, involves five chemical reactions, and from ten to fifteen chemical operations, if all by-products be recovered. If an avoidable loss so small as 1 or 2 percent be permitted in each of these steps, the final yield of carboic acid would be so low that the process might be a commercial failure. Yet carboic acid is one of the simplest products to manufacture.

Many others involve more steps, or steps in which lack of technical skill produces larger loss. For example, a certain product with a normal price of 30

cents per pound has a possible maximum yield of 100 units attainable by extreme care in manufacture. With moderate care the yield is 88 percent, and with only ordinary care the yield drops to 75 percent.

Approach to 100 percent technical efficiency is not the only requisite for commercial success. The intricate processes yield numerous by-products, some acids and alkalis that must be recovered for use in the process. Others are salts or coal products that must be refined and sold, and for many of these there is no market in the United States.

A network of markets must be created for every one of these by-products, either in the United States, or abroad, if our American coal products industry is to grow and pay reasonable dividends on the investment. It is not sufficient that American consumers acquire the habit of buying chemicals "Made in America." Our chemical industry, to endure, must cover the world's market; indeed, its ultimate success may depend upon an American merchant marine.

The German system of nationalized industry handles this multitude of by-products with military precision, by fitting each one into the particular technical and commercial chink best suited to it, so that all by-products are marketed at or above cost. This permits the main products to be sold at a profit large enough to sustain the normal growth of the plant and to develop new products, without adding new capital, and in addition, pay 10 to 25 percent dividends.

In complete contrast has been, and is, the policy of our Federal government, forbidding such interlocking national co-operation.

The coal products chemical industry is vital to national defense. One source of the extraordinary military strength of Germany is her ability to manufacture ammunition, literally from the air and earth, in unlimited quantity. This ability was created by the chemical industry, which built huge works and trained an industrial army with the scientific knowledge and technical skill necessary to transform the nitrogen of the air and certain coal products into ammunition.

While developing home resources, the German industry bought benzol, carbohic acid and other crude coal products from England, thus absorbing England's commercial and military strength. Meanwhile we were more backward than England, for we were so quick to grasp the opportunity presented by German dyes and pharmaceuticals at low prices, that we did not even take the trouble to produce enough crude coal products to export.

In 1915 we built many ammunition plants in the United States, every one on an artificial basis, and few of them can make a profit at peace prices. Unless the United States establishes a complete and profitable national coal products industry on a basis to keep abreast with scientific progress, our program of "National Preparedness" will descend to the plane of comic opera.

Nitric acid from the air is one step in such scientific progress. Our supply of nitric acid comes now from nitrate of soda imported from Chili. After the war, if importations are not obstructed, we will receive nitrates and nitrogenous products manufactured in Norway and Germany by fixation of atmospheric nitrogen. Part of these will be for fertilizer, part for explosives. Exhaustion of the Chili nitrate of soda mines will ultimately make the United States wholly dependent upon European supply, unless we manufacture our own nitrates and nitric acid from the air.

Fixation of atmospheric nitrogen as nitric acid will also require several years, even though the Federal government give the manufacture its strongest support. It is the effective end of every explosive, and the first chemical reagent used in the manufacture of aniline, and thence of indigo and others of the most important coal product dyes. Without nitric acid our entire navy, army and coast defense becomes helpless the instant the stock of ammunition is exhausted. Our entire investment in national preparedness will be wasted money if it does not include the manufacture of nitric acid from the air on a scale to render us absolutely independent of foreign nitrates.

The potash situation is a parallel condition. With German potash cut off, we have no supply. Various American sources will be brought into operation, but several years must elapse before we produce all the potash we consume.

A reasonable tariff, if formulated upon national lines, will be of much value in supporting our coal products manufacture. Such a tariff would divide these products into three classes, according to their degree of advancement in manufacture, and levy duties proportionate. The classes would be: First, crude products; second, intermediates; third, dyes, pharmaceuticals and highly refined products.* The duties should be, on crudes 10%, on intermediates 20%, and on dyes 30%, *ad valorem*.

If a specific duty be included it should be at the rate of $3\frac{3}{4}$ cents per pound on the intermediate class and $7\frac{1}{2}$ cents per pound upon dyes and pharmaceuticals, with no specific duty on crude products.

Natural indigo and other natural dyes of vegetable or animal origin should be placed with synthetic dyes, in Class 3. The free list should include coal tar, coal-tar pitch, cresote oil and mineral acids.

There should be an anti-dumping clause to prevent unfair competition, and it must be drafted with care and its working tactfully handled. If it be too drastic, or if handled without good judgment, it will become worthless, or worse, because foreign countries, in retaliation, will inflict anti-dumping penalties upon American goods. We cannot afford to take any chances with American industry now that our export trade in manufactures is becoming better established than ever before in our commercial history.

Compulsory working of patents, in theory, looks attractive, but there has been nothing in the history

of the coal products industry that could have been improved by it in the slightest degree. Compulsory working of patents has been tried in England, France and Russia as recently as 1907, and proven a failure.

As stated by the German authority, Prof. Witt, "the success of a coal-tar dye factory is no longer dependent upon the careful guarding of factory secrets, but upon a systematically arranged plant and the proper distribution therein of the work to be performed, and, above all, upon skillful commercial management, both within and without the factory."

Lack of technical common school education is a further disadvantage from which we suffer. Our system of early 19th century education includes no technical or trade schools, by which, in Germany, the entire population is perfected in 20th century industrial methods. In consequence, it is difficult to secure labor in the United States that will give competent attention to delicate chemical manufacturing operations.

The essentials for creating a complete industry for the manufacture of products derived from coal in the United States are: Co-operation of the American acid and alkali manufacturers with the coal products industry; co-operation of American consumers with American producers, through long-term contracts; the establishment of the industry on a peace scale big enough to make it a fundamental factor in national defense; establishment on a profitable commercial basis of the manufacture of nitric acid, by fixation of atmospheric nitrogen; nationalization, or rather internationalization, of the industry to insure a balanced world market for all by-products; development of a system of 20th century common school and technical school education; finally, maintenance of a rational tariff.

That a larger coal products industry will be established in the United States is certain. The degree of perfection it attains will be in proportion to the extent these requirements for its profitable operation are provided.

The preliminary statement of the general results of the 1914 census of manufactures for the explosive industry, issued by the United States Bureau of the Census, shows that there was a reduction in the quantity of explosives made for sale in this country in 1914 compared with the quantity for 1909, although the value was greater in 1914. The figures for the later year were 482,003,100 lbs., valued at \$30,656,310, and for the earlier year 487,481,252 lbs., valued at \$37,983,868. The quantity decreased by 1.1 per cent, while the value increased by 4.4 per cent. The decrease in amount of explosives manufactured is due to the decreased production of nitroglycerin, which is used largely for torpeding oil wells. The output of nitroglycerin dropped from 28,913,253 lbs., valued at \$3,162,434, in 1909 to 3,560,581 lbs., valued at \$866,120, in 1914, the decrease being 87.7 per cent in quantity and 72.6 per cent in value.

A RAPID PYCNOMETRIC METHOD FOR "GRAVITY SOLIDS" IN CANE-SUGAR FACTORIES.*

By HERBERT S. WALKER.†

Since the introduction into sugar factory control by Deerr¹ of the terms "gravity purity" and "gravity solids," and his demonstration that the determination of total solids by the Brix spindle, while not absolutely accurate except in pure sucrose solutions, when applied to juices, sugars, and molasses at approximately the same dilution (about 15° Brix) yielded, in consequence of consistent error, results fully as valuable for factory control work as the more tedious process of drying to more or less constant weight, this latter method has been entirely abandoned in many factories.

The principal objection to the substitution of densimetric for direct drying methods has been the lack of even relative accuracy in Brix spindle readings; this, as regards accuracy of reading the graduations on the stem of the spindle, has been somewhat improved by several devices suggested in recent years, but there still remain certain inherent errors in the method, due to variable viscosity and surface tension of liquids, which are very difficult to eliminate.

The pycnometer is generally conceded to be an exceedingly accurate means of determining specific gravities, but has thus far found little favor in cane-sugar factories, owing probably to real or fancied difficulty of manipulation and to the extra calculation involved. By means of a few simple modifications, however, a pycnometer determination may be made almost as easily as an ordinary Brix test, and with no calculation other than looking up the Brix in a specific gravity table.

A 100 cc. pycnometer with ground-in thermometer and capillary side arm is used; since all determinations are made at room temperature, the cap of the side arm is thrown away and the arm itself cut off two or three millimeters above the graduation mark, thus facilitating rapid filling to a definite volume.

All calculations could be eliminated by making a pycnometer to contain exactly 100 g. water at a given standard temperature, such as 17.5°, 20°, 27.5° (weighed in air), or 4° (weighed in vacuum), according to the tables one intends to use. The weight of the liquid in the pycnometer would then be 100 times its density as compared with water at that temperature, and if a tare were made to just balance the empty pycnometer, then the weights required to balance the pycnometer filled with sugar solution would indicate the density of that solution without calculation; Brix could then be obtained from the tables, applying the same correction used for Brix spindles in case the determination were not made at exactly standard temperature.

*From The Journal of Industrial and Engineering Chemistry.

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¹Bull. 41, Agr. and Chem. Series, U. S. P. A. Expt. Station.

It is, unfortunately, difficult to obtain a pycnometer of exactly a desired capacity; one a little too large may be reduced by grinding in the thermometer with emery powder, a rather tedious though not difficult process; but a bottle of too small capacity is difficult to enlarge with accuracy.

In such cases it is easiest so to regulate the tare that the additional weights required to balance the pycnometer full of water at standard temperature shall be exactly 100 g., irrespective of the true volume of the pycnometer, *i. e.*, if pycnometer contains 101 g. water at standard temperature and weight of tare equals weight of pycnometer, then

$$\text{Pycnometer} + \text{water} = \text{tare} + 101 \text{ g.}$$

Increasing weight of tare by 1 g.,

$$\text{Pycnometer} + \text{water} = \text{tare} + 100 \text{ g.,}$$

and with pure water this pycnometer and tare will always indicate a density by direct weighing of 1.0000.

With dilute sugar solutions, a pycnometer as much as 1 cc. "off" in capacity will give densities with very little error, but when working with more concentrated solutions a small correction must be made to the observed weights, since the 1 cc. excess capacity which, in the case of pure water, was compensated for by the 1 g. heavier tare, will now weigh more than 1 g. In the above case of a 101 cc. pycnometer with tare adjusted for pure water, if it be used with a solution of 1.3000 density, the extra 1 cc. weighs of course 1.30 grams, while only 1 g. has been compensated for by the excess weight of tare.

Knowing the capacity of a pycnometer, it is a simple matter to make a table of corrections to be applied at different densities. Such a table for a pycnometer containing 101 cc. (a cc. here being considered to be the volume occupied by 1 g. of water at the temperature taken as a standard for the density tables it is desired to use) would be as follows:

Weights used—grams.	100	101	105	110	120	130
Cor. to wts. (subtract)	0.00	0.01	0.05	0.10	0.20	0.30g.

According to the amount of change in tare needed to give a weight of 100 g. with pure water, a table such as the above can be easily constructed for any pycnometer; thus, if it contain 100.30 g. water at standard temperature, make tare equal weight of pycnometer + 0.30 g., and the correction table for different densities is the one given above multiplied by 0.30. The following is an example of pycnometer calibration:

	Grams.
Weight of Pycnometer.....	47.40
Weight of Pycnometer + water at 29° C.....	146.93
Weight of water	99.53

Assuming that this pycnometer is to be used with 17.5°/17.5° tables, and that the average temperature at which it is to be used approximates that of calibration, the change of volume due to expansion of glass may be neglected and the weight of water contained at 17.5° (or its volume in terms of "17.5° cc.") may

be considered to be $99.53 \times (\text{density aq. } 17.5^\circ - \text{density aq. } 29^\circ)$ or $99.53 \times (0.99872 - 0.99598) = 99.80$. If a tare is then made to equal weight of pycnometer minus 0.20 g., or 47.20 g., the weights needed to balance pycnometer full of water at 17.5° will be 100 g., thus giving density direct. The correction for densities greater than 1.0000 will be:

Weights used	100	101	105	110	115	120	125	130g.
Correction (add)	0.00	0.002	0.01	0.02	0.03	0.04	0.05	0.06g.

After looking up the Brix corresponding to any density, the customary Brix correction for temperature of observation must of course be made.

In case the laboratory temperature prevailing were as high as that just noted, it would perhaps be more convenient to use tables calculated for 17.5°/27.5°, in which case the calculation of tare and correction table would be the following:

$$\text{Weight water content at } 27.5^\circ = 99.53 \times (0.99611/0.99598) = 99.57 \text{ g.}$$

$$\text{Weight tare should be } 47.40 - 0.43 = 46.97 \text{ g.}$$

Wts. used	100	101	102	105	110	115	120	125	130g.
Cor. (add)	0.00	0.004	0.009	0.02	0.04	0.06	0.09	0.11	0.13g.

Where it is desired to use a pycnometer for juices or solutions of always the same approximate density, the correction for this density may be incorporated in the tare. In case the above pycnometer were to be used solely with solutions of about 15° Brix or 1.06 density, the correction could be added automatically by making tare 0.02 g. lighter than for pure water, *i. e.*, 46.95 g. instead of 46.97 g. Densities around 15° Brix would then be obtained by direct weighing, with absolutely no correction other than that for temperature subsequently applied to the Brix reading.

The calibration of a new pycnometer, including adjustment of a tare (best made from a small bottle weighted with shot) and construction of a correction table, can easily be done in less than an hour; the calibration of a new Brix spindle at three points on the stem, which is just as necessary, takes considerably more time than this.

An ordinary determination of density of a juice or diluted molasses consists simply of filling the pycnometer to the mark and weighing the centigrams on any ordinary sugar balance, which requires from 3 to 5 minutes, hardly more time than is needed for an accurate determination by means of the Brix spindle.

As regards accuracy, an error of more than 0.01 gram in weighing is unusual; this, at 15° Brix, corresponds to 0.023° Brix, or about one-fourth the average error in reading a Brix spindle.

Dr. F. W. Cunningham of Orange, N. J., has resigned his connection with the research and development work of the Newark plant of the General Electric Company to join the engineering research staff of the Powdered Coal Engineering & Equipment Company of Chicago at which point he is now located. In his new connection Dr. Cunningham will considerably broaden the field of his activities.

CHEMICAL CONTROL OF THE KRAFT PROCESS.*

By OTTO KRESS, Ph.D.†

COMPLETE METHOD OF ANALYSIS OF WHITE LIQUOR.

The following complete method of analysis includes a determination of sulphites and thiosulphates that are ordinarily neglected in the analysis of white liquor but which play an important part in the cook. This is especially true of thiosulphate, which, in the presence of caustic soda, acts to a large extent similarly to sodium sulphide. This method has been worked out and checked by Sidney E. Lunak, of the Forest Products Laboratory, Madison, Wis., and found to be accurate except in the presence of polysulphide, where an error is introduced into the iodine titration. For an ordinary work, this error is not serious enough to be appreciable.

(a) Total Alkali Expressed in Terms of Na_2O .

Two cc. of the solution are withdrawn with a pipette and titrated with half normal acid, using methyl orange as an indicator. The number of cc. of acid used represents the alkali existing in the solution as Na_2CO_3 , NaOH , Na_2S , and $\frac{1}{2}\text{Na}_2\text{SO}_3$.

(b) Soda as $\text{NaOH} + \text{Na}_2\text{S}$.

To 2 cc. of the solution contained in a 100 cc. graduated flask add 20 cc. of a 10 per cent solution of barium chloride and make up to mark with boiling distilled water; shake for a few minutes and allow to settle; cool and draw off 50 cc. of the clear liquid and titrate with half normal acid, using methyl orange as an indicator. The number of cc. indicates the amount of acid necessary to neutralize the NaOH and Na_2S in the sample. The difference between this titration and the previous titration represents the number of cc. it takes to neutralize the Na_2CO_3 and $\frac{1}{2}\text{Na}_2\text{SO}_3$, barium sulphite being practically insoluble in a large volume of water.

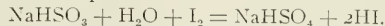
(c) Sodium Thiosulphide + $\text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{SO}_3$.

This is determined by adding the sulphide solution to an amount of iodine within half a cc. of the end point, which can be found by trial. Two cc. of this solution is added to this amount of iodine in about 200 cc. of distilled oxygen-free water and acidified with an excess of acetic acid. The titration is then completed, using starch as an indicator. One cc. of a decinormal iodine solution is equal to .003908 gm. of Na_2S and .003105 gm. of Na_2O . This titration indicates the amount of Na_2S , Na_2S , $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2SO_3 in the sample.

(d) Sodium Thiosulphate and Sodium Sulphite.

To 5 cc. of the solution in a graduated 250 cc. flask add an excess of an alkaline solution of zinc chloride; make up to mark, shake for a few minutes and allow to settle; draw off 50 cc. of the clear solution with

a pipette and neutralize with normal sulphuric acid, using methyl orange as indicator. This converts the sulphites present to acid sulphites. When acid sulphites are titrated with iodine solution the following reaction takes place:



Thus one molecule of acid sulphite on titration with iodine solution liberates acid equivalent to three molecules of sodium hydroxide.

The solution is then titrated with tenth normal iodine solution, using starch as an indicator. It is then decolorized with one drop of sodium thiosulphate solution and titrated to neutral with tenth normal sodium hydroxide solution. The number of cc. multiplied by .0042 gives the amount of Na_2SO_3 in the sample, and this figure divided by .0063 gives the iodine value of the sodium sulphite. Subtract this from the iodine titration previously obtained, which will give the iodine equivalent to the sodium thiosulphate present.

CALCULATION OF RESULTS.

$c-d$ gives the cc. of iodine for sodium sulphide.

$a-b$ gives the number of cc. for Na_2CO_3 and $\frac{1}{2}\text{Na}_2\text{SO}_3$.

1 cc. second normal ($N/10$) $\text{H}_2\text{SO}_4 = .0265$ gm. of $\text{Na}_2\text{CO}_3 = .0155$ gm. of Na_2O .

The titration in (b) expressed in Na_2O , minus the sodium sulphide as Na_2O , gives the Na_2O as NaOH .
1.29 $\text{Na}_2\text{O} = \text{NaOH}$.

1 cc. tenth normal iodine = .0158 gm. of $\text{Na}_2\text{S}_2\text{O}_3$.

BLACK LIQUOR.¹

The examination of black liquor is conducted as follows:

(1) A 50 cc. portion of black liquor is evaporated to dryness in a platinum dish. The residue is ashed over a bunsen burner and the soluble salts are leached out with hot distilled water. The entire solution obtained is titrated with normal sulphuric acid, using methyl orange as an indicator. The number of cubic centimeters of acid required to produce the end point multiplied by 0.62 gives the grammes per liter of total sodium oxide (Na_2O) in the black liquor.

(2) A 100 cc. portion of the same black liquor is mixed with 50 cc. of 10 per cent barium chloride solution in a 500 cc. calibrated flask. The mixture is then diluted to 500 cc. with neutralized or freshly distilled water, free from carbon dioxide and thoroughly agitated. After settling, 50 cc. of the clear supernatant liquor is titrated with tenth normal hydrochloric acid, using phenolphthalein as indicator. The number of cubic centimeters of acid required for the end point multiplied by 0.401 gives the number of grammes per liter of free caustic soda (NaOH) in the black liquor.²

*From Paper, Report of committee of the Technical Association of the Pulp and Paper Industry on standardization of methods of chemical control of the Kraft process. George S. Holmes, Joseph E. Hedin and Otto Kress.

†Chairman of Committee on Sulphate Pulp, Technical Association of the Pulp and Paper Industry.

¹Taken from Bulletin of the U. S. Department of Agriculture No. 80 (Professional Paper), "Effects of Varying Certain Cooking Conditions in Producing Soda Pulp from Aspen," by Henry E. Surface, Engineer in Forest Products, Forest Products Laboratory, Madison, Wis.

²This result must be corrected if Na_2S is found to be present in the black liquor, which can be determined by the method given. Na_2S , on titration with acid, using phenolphthalein as indicator, turns, when half of it is neutralized, to NaSH .

(3) The causticity of the black liquor was calculated from the following equation:

$$\frac{A (0.775) 100}{B} = \text{per cent causticity.}$$

B

In which:

A = the number of grammes per liter concentration of caustic soda (NaOH). (Correct for Na_2S if present.)

B = the number of grammes per liter concentration of total sodium oxide (Na_2O).

Sulphide, if present in black liquor may be determined as follows:

DETERMINATION OF Na_2S_4
(VOLUMETRIC METHOD)³.

(a) *Standard Zinc Solution*: (301.44 gm. for 18 L: 1 cc. = .02 gm. Na_2S .)

10.746 grammes of C. P. powdered (30-mesh) zinc are dissolved in a small excess of nitric acid; ammonia is then added until the precipitate formed is completely redissolved. The solution is diluted to 2,000 cc. Enough ammonia must be present to just keep the zinc from precipitating when diluted to this volume.

1 cc. = .010 gm. Na_2S .

(b) *Ammoniacal NiSO_4 indicator*:

Nickel ammonium sulphate made alkaline with ammonia.

(c) *Manipulation*:

50 cc. black liquor is diluted to 1,000 cc., and 20 cc. (equivalent to 1 cc. original black liquor) is diluted to about 100 cc. with distilled water and the standard zinc solution run in from a burette. The end reaction is determined by noting whether a precipitate of black NiS is formed when a little of the solution being titrated is added to three drops of ammoniacal NiSO_4 indicator on a spot plate or white waxed surface.

RAPID METHOD OF ANALYSIS FOR CONTROL OF WHITE LIQUOR.

(1) Take 5 cc. of the liquor and dilute to 100 cc. with water. Of this diluted liquor take 20 cc. and titrate it with $\text{N}/4$ HCl, using methyl orange as an indicator. This titration indicates the number of cc. of $\text{N}/4$ acid required to neutralize all the alkali present.

(2) Then take 5 cc. liquor and precipitate with BaCl_2 adding enough water to make 100 cc. After precipitation, take 20 cc. and titrate with $\text{N}/4$ HCl, using phenolphthalein as an indicator. After the color changes add methyl orange indicator and titrate again.

Suppose amount of acid used with phenolphthalein indicator to be represented by "A," and the total acid for both titrations by "B," then

A = cc. $\text{N}/4$ HCl equivalent to NaOH plus $\frac{1}{2}\text{Na}_2\text{S}$.

B = cc. $\text{N}/4$ HCl equivalent to NaOH plus Na_2S .

A = (B - A) = cc. $\text{N}/4$ HCl equivalent to NaOH.

2 (B - A) = cc. $\text{N}/4$ HCl equivalent to Na_2S .

Total alkali = cc. $\text{N}/4$ HCl equivalent to Na_2CO_3 plus Na_2S plus NaOH.

Total alkali - (A - (B - A) - 2 (B - A) = cc. $\text{N}/4$ HCl equivalent to Na_2CO_3 .

Total alkali - B = cc. $\text{N}/4$ HCl equivalent to Na_2CO_3 .

Example:

Suppose total alkali = 12.4 cc.

Suppose A = 7.7 cc.

Suppose B = 9.1 cc.

NaOH =

A = (B - A)

7.7 - (9.1 - 7.7) = 6.3 cc. $\text{N}/4$ HCl

$6.3 \times .0474 \times 1000 = 6.3$ grammes per litre.

Na_2S =

2 (B - A)

2 (9.1 - 7.7) = 2.8 cc. $\text{N}/4$ HCl

$2.8 \times .0394 \times 1000 = 27.3$ grammes per litre.

Na_2CO_3 =

Total alkali - B

12.4 - 9.1 = 3.3 cc. $\text{N}/4$ HCl

$3.3 \times .0534 \times 1000 = 43.725$ grammes per litre.

CAUSTIC LIQUOR.

As a matter of every day work to secure a sufficiently accurate knowledge of the causticity of the liquor, take first, 5 cc. of the liquor, dilute to 100 cc. with water and titrate, using methyl orange as indicator.

Place 50 cc. of the liquor in a 500 cc. flask, add about 50 cc. distilled water and precipitate by BaCl_2 , dilute to mark, mix and settle. Withdraw 50 cc. of the clear liquor, or filter and titrate with $\text{N}/4$ HCl, using methyl orange as indicator.

Suppose first titration to have used 12.4 cc. of $\text{N}/4$ HCl and the second 10.5 cc. $\text{N}/4$ HCl. To get causticity divide 10.5 by 12.4 or 84 plus per cent caustic.

Experiments in the use of peat powder on locomotives of the State railways have demonstrated that as heavy trains can be pulled and as good speed be made where this fuel is employed as where anthracite is used, according to a statement issued by the Swedish telegram bureau, which has been received from the secretary of the American Embassy at Stockholm. The statement declares that the powder can technically, as well as economically, take the place of anthracite as fuel for locomotives. The railway directors have decided to undertake the development of this class of fuel by two different methods for purposes of comparison. Two experts have been requested to give complete estimates of the cost of preparing a certain bog for the manufacturer of peat powder, together with estimates of running expenses, by the respective methods. The bog selected is said to be that at Hasthagen, about $1\frac{1}{2}$ miles from the station at Vislanda, with an area of about 500 acres.

³This method has been carefully checked by G. C. McNaughton of the Forest Products Laboratory and found to give good results.

NOTES ON A NEW PROCESS OF BLEACHING.*

By S. F. PECKHAM.

Some years ago a man brought to me some flax fiber and asked me to bleach it by a quick process without injury to the fiber. He said that a certain party that he named claimed to have done it. I said to him, "You will have nothing left but paper pulp," and after some talk he owned up that that was the case.

I knew that about 30 years ago one Charles Toppan had taken out a patent for a bleaching compound of which petroleum and the fixed oil of mustard were the essential ingredients. Great claims were set forth for this mixture, but nothing came of it as there was too little fixed oil of mustard produced in the world to supply the demands of one large bleachery. At that time the only petroleum on the market was Pennsylvania petroleum and it was a well known fact that the crude petroleum and its distillates would dissolve in a solution of soap. A study of this process from all available sources led me to conclude that Toppan's compound, which was originally a lubricating compound, consisted of a fixed mustard-oil soap dissolved in petroleum, and that by varying the proportions his bleaching compound consisted of petroleum or its distillates dissolved in a solution of fixed mustard-oil soap.

A complete study of the chemistry of the fixed oil of mustard led me to conclude that any other pure vegetable oil soap might act in a similar manner. The cheapest oil soap of that description on the market is what is known as cotton-oil soap stock. Having procured some of this, I proceeded to make a solution of Pennsylvania petroleum distillate in a solution of the soap. This oil readily dissolved and on boiling the flax in the solution it came out in a condition to be readily bleached in bleaching solution, but I concluded that the result was not wholly satisfactory as the bleaching solution had to be so strong or the immersion had to be so long that the fiber was tendered.

I then concluded that I would try all the hydrocarbons on the market that came within range of practicability as to price and sufficiency of supply. I first made up a solution of a distillate of California petroleum and on boiling and bleaching the flax it came out very much better in every respect. Reflecting on the fact that California petroleum consists of benzol and its derivatives, while Pennsylvania petroleum consists of paraffins, the idea occurred to me that perhaps still better results could be obtained by using pure or nearly pure benzols.

I found that the different benzols dissolved in soap solution much more readily than the petroleum distil-

lates and that the cleansing effect on the flax fiber was marvelous. Immersion in a very dilute bleaching solution produced a perfect dead-white bleach and left the fiber unimpaired in strength. In fact I had accomplished precisely what the gentleman had asked me to do.

This method can be successfully applied to all vegetable fiber, as linen is the most difficult to bleach of all of them without injury to the fiber.

I have never seen any mention made in chemical literature that benzol and its derivatives are soluble in a solution of soap, nor did I ever hear any statement to that effect. No fixed formula can be designated, as soap is soluble in water in all proportions and the stronger the solution of soap the more benzol the solution will dissolve. The formula used for 100 lbs. of flax was:

Water, 50 gals. Soap, 10 lbs. Benzol, 3 gals.

This was used for a heavy woven linen damask, where for ordinary light cottons, such as "gray cloth," very much less material is necessary. Pure benzol need not be used; any of the light distillates of coal tar, coke oven tar or blast furnace tar, freed from impurities by washing and proper treatment, answers the purpose equally well.

My invention consists of a process of bleaching by substituting for the usual lime and soda boils a single boil in a solution of soap, preferably a pure vegetable oil soap, in which is dissolved a sufficient quantity of benzol (C_6H_6) or its homologs or derivatives, as found in the light distillates of coal tar and similar liquids and in light distillates of some varieties of petroleum, especially that of California, as distinguished from the light distillates of paraffin petroleum. The strength of the solution in both soap and benzol would depend upon the kind and character of the material to be bleached, light cotton fabrics requiring less than heavier cottons, and any cotton less than flax, jute or hemp.

After thorough squeezing and washing to remove the soap solution, the goods or fiber may be bleached in any known chemic. I prefer one of my own preparation consisting of a solution of sodium hypochlorite, prepared by pouring together, cold, a solution of 58 per cent soda ash and a solution of calcium hypochlorite, stirring the mixture and allowing it to settle. Both solutions should be prepared cold, and after mixing the solutions they should be allowed to stand at least 24 days or until all the available chlorine in the calcium hypochlorite shall be found in combination with the sodium and in solution. No formula can be assigned for this mixture as calcium hypochlorite varies indefinitely in strength. The quantities taken should be such that there will be a slight excess of the sodium carbonate. After a great many experiments upon this chemic I have found this method of preparation, which is very unlike any which is laid down in the books, to be the only one that will bring all the available chlorine in the calcium hypochlorite into solu-

*From the Journal of Industrial and Engineering Chemistry, Paper presented at the 8th Annual Meeting of the American Institute of Chemical Engineers, Jan. 12-15.

tion as sodium hypochlorite. It is better to prepare this solution of a strength 3-5° Twaddell, and dilute it to such a strength that an immersion of the goods from 3 to 5 hours will effect a bleach. After washing the bleached goods in water they are soured, washed and calendered as usual.

By this method a complete bleach of either cotton or linen can be had in from one to two working days.

I have described a process of bleaching by which the goods or fiber are prepared for the chemic by boiling in a solution of soap in which has been dissolved a sufficient quantity of benzol or its homologs or its methylated derivatives, either separately or mixed together, as found in coal-tar naphthas and similar liquids and the distillations from some petroleums as above set forth.

The soap which I have used is the cheapest that I know of on the market, as it is a by-product of the refining of cottonseed oil and is used in its crude state without further treatment.

The apparatus used is a Kier with a steam jacket to which is attached an inverted condenser which returns the evaporated hydrocarbons to the Kier. The process was applied on a small scale and thoroughly tested out with the most gratifying results. Of course the goods are singed and sheared as is customary. Goods in small pieces were digested for various periods of time and the resulting goods subjected to a great variety of tests excepting the effects of time upon finished goods. It was found that if the goods were thoroughly dried after thorough washing to free them from soap the effect of the chemic was very much more satisfactory than when they were introduced into the chemic damp, directly from the squeezers. This is not surprising when very dilute solutions of chemic are used as the water remaining in the goods from the squeezers not only dilutes the chemic still further but filled the pores of the goods, thus getting in the way of the chemic and preventing it from doing its work.

An application was made for patent on the above process with the confident expectation that a valuable invention had been perfected, but the officials at the Patent Office in Washington quoted Toppan's and other patents against me and I found that no amount of argument would convince them that there was the slightest difference between the substances designated "Benzine" and "Benzene"—in fact they declared they were identical. Comment is unnecessary in this place upon such an highly unscientific administration of the patent laws.

Venezuela is to have a school of physical, mathematical, and natural sciences according to a recent presidential decree in the *Gaceta Oficial*. The new school is to be established in the city of Caracas, and it will replace the practical work in these sciences which was ordered in a decree issued last November.

A PROPOSED METHOD FOR THE PROFITABLE UTILIZATION OF WASTE SULFITE LIQUOR.*

By HERMAN V. TARTAR.†

The utilization of the waste liquors resulting from the manufacture of paper pulp by the sulfite process is a problem that has received as much careful attention and systematic study perhaps as that of any other waste product of the present day. The technical literature contains reports of many exhaustive investigations on different phases of this problem. Over 150 patents have been secured for utilizing the waste sulfite liquor. In spite of all this experimental work, however, this material is still classed as a waste. Considering the amount, it is one of the most valuable waste materials known to industrial chemistry.

Most of the paper mills get rid of the waste liquor by emptying the same into streams. An estimate of the quantity of this material discharged annually into the streams of this country is given in the following table taken from Water-Supply Paper 226 of the United States Geological Survey:

AMOUNT OF SULPHITE WASTE LIQUOR DISCHARGED INTO STREAMS OF THE UNITED STATES DURING 1906.

	Million gallons.
Maine	560,000,000
Massachusetts	45,000,000
Michigan	175,000,000
New Hampshire	380,000,000
New York	1,000,000,000
Ohio	41,000,000
Oregon	52,000,000
Pennsylvania	217,000,000
Virginia	84,000,000
West Virginia	89,000,000
Wisconsin	540,000,000
All other states	44,000,000
	3,227,000,000

When one takes into account that of this enormous quantity of liquor discharged annually into streams there is 10 per cent by weight, or more than 2.5 billion pounds of solid matter, largely organic, it must be conceded that its disposal is a problem of no small magnitude. In fact, the pollution of streams in this manner is one of the most serious water pollution problems confronting this and several foreign countries. "The seriousness of the problem is the direct result of two factors—the tremendous volume of such waste liquors and their high content of organic matter of extremely undesirable character."

Besides the usual objections to the addition of organic matter to streams, some of the paper mills of Oregon, and other western states have met with the further objection that the sulfite liquor may be toxic and poisonous to fish. This latter objection is an important one when the waste liquors are discharged into streams where the salmon canning industry has reached considerable proportions.

At the suggestion of the Crown Williamette Paper Company of Portland, Oregon, Professor Charles

*From The Journal of Industrial Engineering Chemistry.
†Agricultural Experiment Station, Corvallis, Ore.

Marchand, of the Pernot Laboratories of the same city, decided to devote some of his time and attention to the utilization of waste sulfite liquor. He began work during the summer of 1914 and carried out his investigations intermittently for some months. He finally succeeded in devising a process which, from small laboratory tests, indicated that it is possible to make alcohol profitably from the waste liquor and also to detoxicate the liquor so that it is not harmful to fish after it is diluted somewhat with water. The paper manufacturing company mentioned above desired to try the process on a scale sufficiently large that the results obtained would give some idea of its actual commercial value. The requirements specified by internal revenue laws regulating alcohol distilleries, however, are such that an experimental distillery could not be arranged for by the parties concerned without much inconvenience and considerable expense. The federal laws do accord to the agricultural experiment stations special privileges which make the establishment of an experimental distillery a comparatively simple matter. For this reason, the agricultural experiment station of this state was requested to take part in the work and establish what is known under the federal laws to be an "agricultural experiment distillery" for making alcohol for denaturation only.

Because of the great importance of the problem to this state and this country in general, the experiment station authorities decided to take up the work. An "agricultural experiment distillery" with proper stills, fermenting vats, etc., for handling 500 gallons of liquor, was established at the plant of the Crown Williamson Paper Company at Oregon City, Oregon, and Professor Charles Marchand, Mr. Vance P. Edwards and the author undertook the necessary experimental work. Practically all of the details of the experiments were carried out by Professor Marchand and Mr. Edwards, the writer having charge of the experimental plant and acting largely in an advisory capacity. The following is a brief description of the process used in the experiments:

The amount of sulphurous acid, free and combined, in the waste liquor is first quantitatively estimated by acidifying a known quantity of the liquor with sulphuric acid and then distilling the sulphur dioxide into a definite quantity of sodium hydroxide and finally titrating the excess of alkali. A determination of reducing sugar is also made, after the removal of tannin, by the usual reduction method with Fehling's solution. Sufficient diluted commercial sulphuric acid (the concentrated acid diluted 1 to 3) is then added to the liquor taken for treatment to be the reacting equivalent of the free and combined sulphurous acid present. This will give an excess of sulphuric acid because a portion of the sulphurous acid in the liquor is present as free acid.

The liquid is then evaporated, preferably *in vacuo*, to half its volume at a temperature not exceeding 85°

C. A temperature higher than this may destroy some of the fermentable sugar. By this evaporation all but a trace of the sulphurous acid is removed. The sulphur dioxide driven off by the evaporation may be passed into milk of lime and magnesia to prepare new cooking acid.

The last trace of sulphurous acid remaining in the evaporated liquor is transformed into sulphuric acid by means of an oxidizing agent. This is a very vital step in the process because it finally effects the complete removal of sulphur compounds which are anti-ferments. Potassium permanganate seems to be one of the cheapest materials which can be used for this process.

After the oxidation of the remaining sulphurous acid is accomplished, the liquor is then neutralized with calcium hydroxide, using litmus paper to indicate the point of neutrality. Great care should be taken not to add an excess of the milk of lime; the liquid is next allowed to cool and is drawn off from the calcium sulphate, which settles out, into the fermenting tank.

The concentrated liquor contains, as a rule, about 6 per cent of fermentable sugar. Finally ordinary brewers' yeast is added and the fermentation is carried on for 40 to 60 hours at a temperature around 27° C. During the fermentation the liquid is agitated (or a little air is forced through it) to favor the process; the former method is preferable, because in the latter there is some loss of alcohol.

Finally, the alcohol is distilled off in the usual manner by means of a continuous still.

Several experiments were carried out by the above described process making some variation with the length of the time of fermentation, the acidity of the liquor fermented and the concentration of the liquor. The results of these experiments are summarized in Table I.

The figures for dextrose are somewhat high. Under the conditions which prevailed the experimental work had to be accomplished in a limited time and consequently in making the determination of fermentable sugar the tannin was not removed previous to the reduction with the Fehling solution. Since the tannin also reduces Fehling's solution, the results are a fraction of a per cent too high. The results are comparative, however, and that is all that is claimed. In Experiments 1, 2, 3 and 4, the fermentation was carried out under very slightly alkaline conditions, while in 5 and 6 the treated liquor was slightly acidified. The results obtained indicate that the fermentation proceeds much better under slightly acid conditions. The proper conditions may be obtained by adding 1 part of sulphuric acid to 1,000 parts of the liquor obtained from the neutralization with lime.

The liquor is easily fermented after treatment; the process appears to effect the complete removal of the

sulphur compounds which act as antiferments. No special yeast is required as is the case in some of the proposed processes of securing alcohol from sulphite liquor. Ordinary brewers' yeast was used with good results in all the experiments which have been tried. The fermentation takes place rapidly and, under the conditions here reported, it is complete in about 48 hours. In some of the experiments a small portion of the liquor was allowed to ferment over 100 hours without any further production of alcohol.

The treatment of every 500 gallons of liquor required about 23 lbs. of sulphuric acid and 0.5 ozs. of potassium permanganate. The apparent percentages of fermentable sugar in the liquor before and after concentration indicate that the digestion with sulphuric acid increases the quantity of fermentable sugar; there seems to be no other way of accounting for the increase in sugar during the concentration of

It was practically impossible with an experimental plant of the size used in the work here reported to get at the cost of producing alcohol on a large plant basis. Careful and conservative estimates indicate, however, that the production of alcohol by the above described process is an economic possibility. The experiments made showed that approximately 5 cents worth of sulphur was recovered for each gallon of alcohol produced.

Several other methods have been proposed for the manufacture of ethyl alcohol from waste sulphite liquor. Of these, the one which compares most favorably is the Ekstrom¹ process. It is now being used in Sweden and at one large plant in this country. In this process the sulphites are partially removed by precipitation as the calcium salt. The liquor is then concentrated and fermented by a special sulphur-resisting yeast. The method here given, however, ap-

TABLE I.—RESULTS OF FERMENTATION EXPERIMENTS WITH THE TREATED WASTE SULPHITE LIQUOR.

Expt. No.	Gallons of liquor treated.	Gallons of liquor after treatment.	Per cent concentration.	Gallons of concentrated liquor after fermentation.	Fermentation period, hours.	Fermentation temp., °C.	Per cent Fermentable Sugar.				Percentage of volume from original liquor.		
							In original liquor.	In concentrated liquor before fermentation.	In concentrated liquor after fermentation.	Per cent of sugar fermented.	Abs. alc.	90° proof alc.	Theoretical yield abs. alc.
1	190	200	40.8	391	60-72	23.3-25.5	2.80	5.75	2.71	3.04	(a)	(a)	0.64
2	1270	432	31.0	391	60-72	23.3-25.5	1.70	5.40	2.60	2.80	(b)	(b)	0.49
3	488	245	50.2	181	36-56	18.3-24.0	3.33	6.66	3.43	3.23	0.80	0.84	0.84
4	505	253	50.1	181	40-50	22.2-24.4	2.98	7.17	3.19	4.28	0.76	0.80	1.11
5	552	237	43.0	186	36-46	20.0-22.2	2.91	6.88	2.30	1.58	0.79	0.83	1.11
6	515	259	50.3	200	45-55	23.3-25.0	3.02	7.66	2.44	5.22	0.86	0.90	1.36

(a) The distillation was lost because of imperfect apparatus.

(b) Acetic acid fermentation set in before distillation.

the acidified liquor. The yield of alcohol was somewhat low considering the theoretical yield. The low yield was undoubtedly due to volatilization permitted by the imperfectness of the apparatus used. The writer believes that a yield of 1 per cent of absolute alcohol could be obtained with a properly constructed and controlled plant.

A few tests, made to ascertain the quantity of sulphur dioxide removed by the sulphuric acid treatment, indicated that the quantity of sulphur dioxide liberated was approximately 0.8 per cent of the original liquor.

The solids of the liquor are reduced nearly 30 per cent by the above described process and the liquor remaining after the distillation of the alcohol is, when somewhat diluted, apparently not noticeably toxic to fish. Experiments were tried placing goldfish in the diluted liquor; the fish seemed not to be injured by the liquor. Similar experiments made using the untreated liquor caused the death of the fish in a few seconds. Although the treated liquor is detoxicated, it must still be considered a source of stream pollution because of the large amount of organic matter present. Further experiments have not been made to ascertain if the liquor remaining after the fermentation can be utilized profitably.

pears to have several advantages over the Ekstrom process.

On the whole, the above described process appears to be sound. The reactions brought about are definite, simple and easily controlled.

CONCLUSIONS.

1. A simple and easily controlled process has been proposed for the economic production of alcohol from waste sulphite liquor.

2. The process also detoxicates the sulphite liquor so as to make it, when diluted in the usual amount, practically harmless to fish.

A preliminary report issued by the United States Bureau of Census, Department of Commerce, gives the cotton consumed in the United States during February, 1916, as 540,711 bales and for the seven months ended February as 3,615,365 bales. There were 1,985,045 bales on hand in consuming establishments on February 29, compared with 1,654,100 bales on the same date in 1915, and 3,971,316 bales in public storage and at compresses, compared with 4,075,435 bales in 1915.

¹For references to patents see Chem. Abs., 8 (1914), 1669.

METALLURGY

ELECTROLYTIC ANTIMONY REFINING.*

By ANSON G. BETTS.

It is already known that antimony may be electrolytically deposited in a very satisfactory mechanical condition from the fluoride solution, and that the deposit does not carry down antimony salt with it, as the deposit from the chloride solution is apt to do. I have shown that the fluoride solution, for an easy anode reaction, should not contain sulphates or other oxygen acids, or their equivalents, because the anode reaction tends to the formation primarily of antimony sulphate, for example, which quickly decomposes into an insoluble basic sulphate.† This material insulates the anode surface, and by raising the electromotive force helps the solution of the less-readily attacked constituents of the anode. The fluorine anion is relatively sluggish, and in presence of the more easily transported sulphion, for example, forms at the anode a small proportion only of the directly soluble antimony fluoride. To achieve at once complete solution of the anode as fluoride, it is necessary to exclude all other anions from the solution.

It has not been known how the impurities of the antimony anodes will behave. Lead can be expected to form lead fluoride, which by reason of its insolubility may remain largely in the anode slime. Bismuth also makes an insoluble fluoride in the presence of free hydrofluoric acid, and in the absence of stronger acids, and may be expected to remain in the anode slime, if the solution is rightly proportioned.

Silver stands about 0.6 volt below antimony in the scale of electromotive forces of solution, and could only be expected to remain in the anode residue as metal; gold would, of course, act likewise, and for the same reason.

Copper is readily dissolved as anode in a fluoride solution, and stands so near antimony in the scale that it might seem unlikely that copper would remain undissolved if there is the usual polarization voltage at the anode surface of 0.1 to 0.2 volt, even with a pure fluoride solution. It will be shown by what follows that generally copper does not dissolve at the anode, and knowing the ready solubility of copper fluoride, we can be quite sure that the copper remains in the slime in the metallic condition.

Arsenic is also very near to antimony in the electrochemical scale, and is thought to have a higher deposition voltage than antimony. One would expect

that arsenic would dissolve from the anode, and not depositing so rapidly as the antimony, would accumulate in the solution until by virtue of its increasing concentration it finally deposited in the cathode metal as fast as it dissolved from the anode. This expectation was not realized experimentally.

The first experiment was made in a paraffined wood cell holding about 1,500 c.c., fitted with a stirrer which at times stopped working and detrimentally affected the experiment, but not seriously.

The anode was 1x4.25x6 inches (2.5x10.5x15 cm.) and weighed 3,055 grams. Analysis showed it to contain:

	Per cent.
Silver	0.092
Antimony	74.79
Arsenic	11.88
Lead	3.98
Copper	3.25
Bismuth	2.58
Iron	0.16

The solution was made up to contain in 100 c.c., 10 grams of antimony as trifluoride, besides potassium fluoride and hydrofluoric acid in the proportions given by the formula $\text{SbF}_3 \cdot \text{KF} \cdot \text{HF}$. The mixture crystallized partly, so the solution was not as strong as was intended.

The cathodes were of copper, spaced about one inch (2.5 cm.) from the surfaces of the anode. The current used varied from two to three amperes, and mostly it was very near 2.1 amperes, corresponding to a current density of 6.6 amperes per square foot, or 73 amperes per square meter. The electromotive force was near 0.6 volt, but this increased after two or three days, as the slime layer grew thicker. The slime was removed occasionally, to prevent this undue voltage with the consequent increased solution of impurities from the anode that one would expect. The deposited metal was removed from the cathodes frequently, and the percentage of impurity it contained was determined. No appreciable quantity of impurity was found in any of it, except about 0.35 per cent of Pb, and some As. The principal results are shown graphically in Fig. 1. It was noted that the percentage of As in the metal deposited only varied a little, depending on the rate of circulation to a slight extent, but more on the current density and on the amount of slime on the anode.

The amount of arsenic in the solution at all times was small, the amount being plotted in Fig. 1. Comparatively, the As is far more concentrated in the cathode metal than in the solution, which shows it to be more readily precipitated than antimony. As/Sb in cathode metal approximated to 0.065, while As/Sb in solution approached 0.016.

*Paper prepared for the 25th General Meeting of the American Electrochemical Society, in San Francisco, Sept. 16-18, 1915.

†Trans. Am. Electrochem. Soc., 8, 187 (1905).

The deposited metal was at all times hard, solid, and non-projecting.

The principal conclusions to be drawn are: (1) there is no difficulty in eliminating lead, bismuth, and copper under these conditions, which are rather severe with so low a proportion of antimony in the anode metal; (2) the solution does not become contaminated with impurities; (3) the physical condition of the deposit is all that could be desired; (4) the required current density is less than is desired and generally used for other metals, and the voltage is a good deal

quantity of fresh antimony, and was cast into a new anode, which should have had about the following composition. (It was not analyzed.)

	Per cent.
Antimony	87.5
Arsenic	5.95
Lead	2.0
Copper	1.65
Bismuth	1.3
Iron	0.16

The solution and cathodes were the same as were used in the former experiment. The current density was about 6 amperes per square foot, and electromotive force 0.6 to 0.65 volt. The electrolysis was continued for about 36 hours, and 250 grams of the anode was decomposed, while 221 grams was deposited on the cathodes. The anode slime was very soft and readily removed, and did not interfere with the solution of the metal underneath, as was the case in the first experiment.

The electrolyte was analyzed at intervals for As, which was found to amount to 0.06 gram As per 100 c.c. during the entire experiment. The first 143 grams deposited contained As, 4.23 per cent; Cu, Pb, Bi, none, and the 78 grams following contained 13.9 per cent As and 25.3 per cent Sb.

The conclusions are these: (1) with an anode of this composition the electrolysis goes smoothly, and there is no need of scraping the anode slime from the anodes; (2) a larger proportion of the arsenic goes over into the cathodes, viz.: 60 per cent as against about 40 per cent of the total As in the first experiment. The deposit was physically good, perhaps a little better than before. Cu, Pb and Bi may be separated from antimony in this way.

When a solution of arsenious chloride is heated with metallic copper, a black arsenide of copper is precipitated on the copper. To learn whether the presence of copper would tend to retain arsenic in the anode slime as an arsenide of copper, thus yielding a purer antimony deposit at the cathode, an anode was made containing about

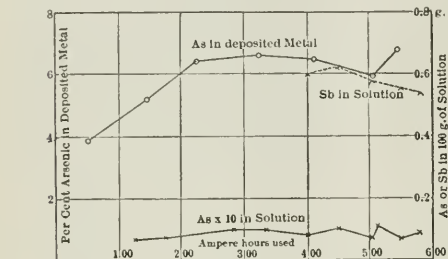


FIG. 1.

higher; (5) only about half the arsenic could be kept in the anode slime.

The additional analyses which were made in connection with the experiment are:

	Slime.						
	1	2	3	4	5		
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		
Arsenic	19.6		18.06	17.46			
Antimony	28.1		21.17	24.57			
Lead	15.4		14.3	14.2			
Copper	10.6		16.3	16.0			
Bismuth	9.85	13.5	13.1	11.7			
Iron	Trace						
Silver							
Amount	48 gr.	30 gr.	39 gr.	46 gr.	36 gr.		
	Deposited Metal.						
	1	2	3	4	5	6	7
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Arsenic	3.89	5.18	6.36	6.59	6.45	5.92	6.81
Antimony	94.73	93.32	91.97	91.33	91.88		
Lead					0.35		
Copper					None		
Bismuth					None		

Samples of the cathode metal for analysis were fused under KCN, before the analyses. The weight of anode decomposed was 853 grams, and of metal deposited, about 675 grams. There was 199 grams of slime produced. Some metal was found in the bottom of the cell.

In the preceding experiment the anode contained a larger percentage of impurity than is usual in electrolytic refining of metals. As it was impossible to conclude that with an anode containing less impurity arsenic would remain entirely, or in larger proportion, in the anode residue, another experiment was necessary.

Part of the old anode was melted with an equal

	Per cent.
Antimony	84.8
Arsenic	5.4
Lead	1.8
Copper	6.65
Bismuth	1.2

In refining this anode, the solution and conditions were the same as in the preceding experiment, except that the stirring was even more vigorous this time. At the end of 31 hours, the solution contained 0.045 per cent As and the deposited metal 3.15 per cent As, with only a trace of copper.

The result shows the effect of copper in holding back arsenic in the slime to be certainly small, if there is any such effect at all.

Following up the discovery that arsenic tends to deposit from the fluoride solution more rapidly than antimony, in proportion to the quantities present, it becomes important to know if in depositing antimony from the fluoride solution containing sulphuric acid, with an insoluble lead anode, as is sometimes done in

treating Pb refinery anode slime, the arsenic present in the solution could not be collected with the first part of the antimony, thus producing the latter, and perhaps greater part of the antimony in pure form.

Fourteen hundred c.c. of solution was used containing about 124 grams of antimony and 5.3 grams of As as trifluorides, one or two grams HF, and 65 grams H_2SO_4 ; or per 100 c.c. Sb 8.85 grams, As 0.38 grams, HF about 0.1 gram, H_2SO_4 4 grams. The solution was electrolyzed at the ordinary temperature with two copper cathodes, having an active area of 24 square inches (150 sq. cm.), and with a lead anode, cotton-covered, having an active area of about 2.5 square inches (15.6 sq. cm.). The current was 1.2 amperes, or a cathode current density of 7.2 amperes per square foot (80 per sq. m.).

Analysis of the solution was made at intervals for antimony and arsenic, the difference between two consecutive analytical results showing the quantities deposited. The results are plotted as Fig. 2, in which the curves show grams of antimony, and twenty times the grams of arsenic per 100 c.c.

Only one analysis of deposited metal was made, that of the first 9 grams deposited, which contained 5.0 per cent As. The proportion of As to Sb at the start was 4.3 per cent.

Referring to the figure, the Sb and As curves up to 34 ampere hours show that the Sb and As are depositing out in very nearly the same proportion as they exist in the solution. If any separation of the two were practicable in this way, the favorable conditions of this experiment, low current density, and very good circulation, should show it. During the experiment the rate of circulation was changed to see if it made any difference, but none was detected.

After about 34 ampere hours of current passed, and it was seen that no practicable separation of As and Sb was indicated with this solution, copper sulphate was added to the solution, to see if copper in depositing would have any tendency to carry As out with it. Furthermore, copper is usually present to some extent in the antimony fluoride solutions resulting from the treatment of lead-refining slimes by hydrofluoric acid, and in removing that copper by electrolysis with a very low density, arsenic might be found to separate with it.

The conclusion of the experiment showed that copper has a tendency to do this, but the effect is too small to be of any use.

The continuation of the Sb curve in a dotted line is derived by subtracting from the antimony found by analysis the antimony equivalent of the copper added.

Calculating the ratios of antimony and arsenic in the deposited metals and in the solution, in the beginning of this experiment they are respectively about 19.1 and 23.1, so that the relative speed of deposition of antimony and arsenic in proportion to the amounts present is about 1 : 1.2.

With the solution used in the antimony refining

experiments, the principal difference being that the refining solution contained no sulphuric acid, the corresponding ratio is about 1 : 4.2. The presence of sulphuric acid interferes to a large extent with the tendency toward separation of the two elements.

With such a refining solution as that used in the first experiment described, there is sufficient difference in the behavior of arsenic and antimony to make possible a differentiation of the deposited metal into two parts, one a good deal lower in arsenic and the other higher, by alternately causing the refining solu-

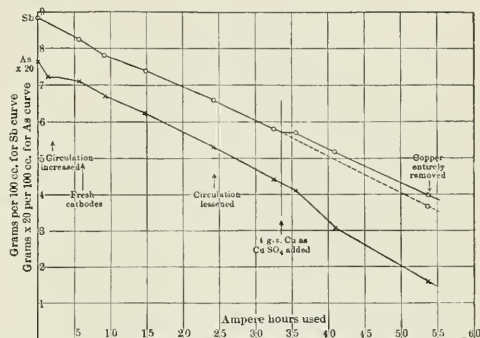


FIG. 2.

tion to circulate rapidly and remain at rest. If the solution were electrolyzed quietly, keeping the anode away from the cathode, and removing a large proportion of the metal from the solution in contact with the cathodes, the deposited metal should contain only about 1 per cent of As instead of 6 per cent, as the total quantity of As present in the solution is so small. If the solution is then rapidly circulated so that the As brought into solution from the anode could be quickly brought to the cathodes, the proportion of As deposited should be much greater than 6 per cent, perhaps as high as 25 per cent.

The simplest way in which to carry out this idea of producing two quantities of antimony, one very high and one very low in arsenic, is to cause the solution to pass in turn through a cell with strong agitation, and one with as little agitation as possible, preferably arranged so that the heavy solution running down the anode surface could be collected in the bottom of the quiet cell, and siphoned out into the agitated cell.

The apparatus used consisted of one main wooden cell 38 cm. deep by 12.75 cm. by 20.3 cm., with a capacity of about 10 liters, and a series of four auxiliary cells 12.9 cm. deep by 7.75 cm. by 7.75 cm., with a total capacity of about 3 liters.

The main anode, about 1.8 cm. thick by 15 cm. by 30 cm., was suspended in the middle of the main tank, between two copper cathodes.

The first of the small cells, through which the solution from the main tank passed, contained one anode

of the same composition as the main anode, and a copper cathode, the active anode or cathode area being about 0.8 cm. by 10 cm.

In the other three tanks anodes of pure Sb, and Cu cathodes, were used, of the same size as those in the first of the small tanks. The alloy to be refined contained:

	Per cent.
Antimony	84.0
Arsenic	5.4
Copper	3.6
Lead	3.7
Bismuth	1.1

The solution was made to conform to the formula $\text{SbF}_3 \cdot \text{NaF} \cdot \text{KF} \cdot \text{HF}$, and should have contained 4.4 grams Sb, 1 gram Na, 1.4 grams K, and 0.8 gram HF per 100 cc. A small quantity of salts crystallized out and a very little solution was spilled, so the solution was undoubtedly somewhat weaker and contained at the end of the experiments only 1.8 per cent Sb. This lowering would, of course, result from the conversion of the lead in the anode to lead fluoride with the reduction of the corresponding amount of antimony.

Some difficulty was experienced in regulating the flow of solution through the tanks, and the stirrers sometimes stopped during the night.

With an electromotive force of 1.35 volts the large tank used (at about 17° C.) 8.5 amperes, and the four small tanks in multiple about 15 amperes, or current densities of respectively 1.2 and 0.4 amperes per square decimeter (12 and 4 per sq. ft.).

The large tank was fitted with a distributor, so that the heavy solution flowing in from the four small purifying tanks should mix with the light solution at the top of the large refining cell.

The heavy solution running down the anode collected in the bottom of the tank and was continuously removed to the purifying tanks through a rubber tube.

During the first experiment the heavy solution at the bottom of the refining cell and in the purifying cells contained about 6.2 per cent Sb, and the solution at the top of the refining cell 3.3 per cent Sb.

The character of the deposit in the four purifying cells was different, that in the first cell especially being darker, duller and less crystalline, and containing more As, as was expected.

After three days the solution in the first three of the purifying cells contained:

No. 1	0.148	per cent	Arsenic
No. 2	0.133	"	"
No. 3	0.122	"	"

The purification was evidently less complete than could be inferred from the fact that the solution in the first refining experiment contained only about 0.05 per cent As.

After five days the upper three-quarters of the main cathode was collected and melted separately from the bottom quarter. The upper 660 grams contained 3.0 per cent As and the lower 210 grams contained 3.4 per cent As. To the solution was then added enough NaF to correspond to the formula $\text{SbF}_3 \cdot 2\text{NaF} \cdot \text{KF}$.

HF. The solution crystallized a little, so it was taken out, filtered, mixed and analyzed, showing it to contain 0.0 per cent As, and put back.

After five days more 1,060 grams of cathode metal was found to contain 3.18 per cent As.

The following analyses are of the slime produced in the first five days, the second five days, and that taken from the first small cell:

	First Slime Per cent.	Second Slime. Per cent.	Slime in Small Cell. Per cent.
Arsenic	8.2	8.17	8.5
Antimony	7.16	7.94	16.7
Lead	26.9	28.1	
Copper	30.1	26.2	
Bismuth	6.53	5.4	

Thinking that a diaphragm might keep the impure anode solution in the refining cell away from the cathodes, a muslin diaphragm was used, reaching nearly to the bottom of the cell. The diaphragm was of two or three thicknesses, spaced one-half inch (1.25 cm.) in the clear from the anode surface. The current was reduced to 5.5 amperes for the large cell and 1.5 amperes for the four small cells in multiple. After six days electrolysis the following figures were obtained by analysis of the products:

	Grams.	Per cent Arsenic.
Upper third	240	3.4
Middle tank	275	3.3
Lower third	260	3.3
Small tank No. 1	59	4.6
Small tank No. 2	87	3.9
Small tank No. 3	75	3.9
Small tank No. 4	100	3.9

The absence of a diaphragm was evidently not the weak point in the first part of the experiment, as the result was practically the same either way. The percentage of As in the metal deposited in the four small tanks was evidently much less than indicated from the ratio of 1:4.2 for As in metal found in the first experiment. The difference must be due to a difference in the temperature, current density, or composition of the solution.

Another run of four days with the addition of four grams HF per liter yielded products analyzing as follows:

	Grams.	Per cent Arsenic.
Main cathode metal	430	3.6
Small tank No. 1	17	6.6
Small tank No. 2	23	6.3
Small tank No. 3	20	6.1
Small tank No. 4	20	5.8
Total of small tanks	80	6.05

The improved, but still unsatisfactory result, is believed to be due to the presence of more HF in the solution.

The solution (now thrown away) contained 1.8 per cent Sb and 0.06 per cent As giving a ratio calculated as before of 1:2 since

As in solution As in metal
----- = 0.033 and ----- = 0.066. Ratio
Sb in solution Sb in metal
is 1:2.

It was concluded that a study of the ratio

As in solution	As in metal
Sb in solution	Sb in metal

with varying solution composition, temperature, current density, and perhaps other factors is necessary for successful refining by this method.

Experiments were then made to determine the effect of temperature on the amount of As passing over into the cathodes. As there is a counter e.m.f. even with the fluoride solution, sometimes as high as 0.2 volt, it might be possible by raising the temperature to reduce the anode e.m.f. to a point where antimony but not arsenic could be dissolved.

The solution used contained, in 100 cc., 3 grams NaF, 11 grams SbF₃ and 1 gram HF. Three small rubber jars were arranged as electrolytic cells at temperatures of 30°, 40°, and 50° respectively. The current varied from 1 to 1.4 amperes, correspondingly to a current density per square foot of 14 to 20 amperes with an e.m.f. per cell of about 0.9 volt. After 43 hours electrolysis the experiment was discontinued with these results:

30° cell short circuited, 35 grams deposited, in smooth condition at the bottom and rough and flaky on top.

40° cell, 54 grams deposited, rather smooth and even throughout.

50° cell, 45 grams deposited, in still smoother condition.

The deposits were melted and analyzed for As, with these results:

Temperature.	Arsenic. Per cent.
36°	3.5
40°	3.6
50°	3.9

I tried the purification of antimony from arsenic by crystallizing the melted metal analogously to the purification of lead and bismuth by crystallization. Numerous experiments with antimony-arsenic alloys containing from 3 to 8 per cent of arsenic gave in all cases crystals and liquid portions containing the same percentages of arsenic.

The alkaline sulphide solution of antimony was tried as a refining medium. The solution was made by dissolving 30 grams of SbF₃ in 500 cc. sodium sulphide solution of specific gravity 1.10. The solution was electrolyzed warm with the same composition of anode as used in the last preceding refining experiments.

After 24 hours' run the cathode deposit averaged 1.0 per cent As and after 48 hours 2.1 per cent As.

Returning to the original idea of refining in the usual way, with the fluoride solution, some of the refined antimony containing about 3 to 3.5 per cent arsenic was cast in the anode, and again refined in the same way. About half of the arsenic remained in the anode slime. By several refinings the arsenic may probably be eliminated.

The most positive reaction noted in these experiments is that due to the composition of the solution.

An increase in HF is highly beneficial and the presence of sulphates or sulphuric acid is shown to be objectionable. It is likely that the hydrofluoric acid may have contained traces of sulphuric or fluosilicic acid, and the negative results might have been traced to that cause. The effect of alkaline fluorides and ammonium fluoride should be studied, also.

A successful method of electrolytic refining of antimony should receive technical application, inasmuch as present methods do not save the gold frequently present and are incapable of making a product of a high and uniform grade at all comparable to the copper, lead and silver on the market.

MAGNESIUM.*

By W. M. GROSVENOR.

The alkali earth division of the second group in the periodic table consists of more or less soft, white metals and all show great avidity for oxygen, decomposing water more or less readily. None except aluminum has found large commercial use but of the others magnesium leads the list by a long distance. Its chief uses are:

1. Scavenging alloys, *i. e.*, clearing up oxides of other metals and making far denser, cleaner, stronger and more homogeneous alloys. It is valuable in aluminum, nickel, copper, brass, bronze, etc., and special steels, because of its intense avidity for both oxygen and nitrogen.

2. Alloying itself, with aluminum or aluminum containing traces of one or more of the other metals Cu, Ni, Zn, Pb, Bi, Sb, Fe, etc. Magnesium greatly modifies crystallography and physical properties and alloys readily with most metals and melts at a convenient heat.

3. Illumination, as in military uses, for shrapnel trailers, star bombs, flare lights, etc., and in photography for flashlights. Its easy inflammability (about 800° C.), the high heat of combustion (134,000 cal.), the relatively low heat of vaporization (1100° C.), the intensely white oxide produced and the high temperature of volatilization of this oxide, are the essential factors.

How much is used? Records of imports for the year prior to the war indicated 38,000 lbs. About 100 lbs. a day, therefore, seemed to be a safe production to undertake. Prices before the war had been very steady around \$1.45 per lb., but it seemed reasonably certain the cost need not exceed \$1.00 per pound, and after the war began the prices being paid for remnants of imported lots quickly rose to \$2.50. Some of the first demands here were from wholly unexpected quarters, in surprising amounts and at amazing prices. The most urgent, almost pitiful demands, came from quarters that were not even suspected to

*Address Feb. 11 before the New York Section of the American Electrochemical Society, in joint session with the New York Section of the American Chemical Society, Chemists' Club.

be interested in the least. One consumer has contracted for 24,000 lbs. and another 15,000, these two alone taking for strictly domestic use more than was supposed to be the total importation. There are at least three other buyers of similar quantities but exact amounts are not yet established. Sales are largely made by yearly contract and even at present prices the consumption for strictly domestic use is about 50 tons. We found that a great deal of the material was being imported under other names and most carefully disguised—secrecy being preferred to economy. Prices as high as \$10.00 per pound were gladly paid at first for domestic product. For some months then the prices jumped around from \$5.00 to \$7.50 but every effort was made to reduce conditions to some sort of order by dealing direct with the consumer. This was partly the result of a deliberate policy for better and more intelligent service of the consumer's precise demands as to quality and delivery, but partly also the result of meeting quite unexpectedly the competition of our own product at prices from 25 percent below to 50 percent above the prices we had made. Some of New York's clever war goods brokers added 10 percent each through a chain of four or five middle men. Others assumed direct quotations to have already been through this process and knocked off 20 percent, trusting that "real cash business" would squeeze down the middle men they supposed to exist and still leave 5 percent for the real seller. Now, however, for a number of months the price has been practically fixed at \$5.50 per lb. of "Guaranteed 99%," actually about 99.5 percent. Occasionally a lot that has been picked up in the antebellum market for speculation is let go at lower figures, or a lot of lower grade material comes on the market from abroad, but there is practically no volume of these sales.

In spite of the beautiful appearance of the German bars they rarely exceeded 98 and often fell as low as 96 percent. The process of extrusion conceals impurities by drawing them out into minute threads. It is safe to say that the regular commercial grade of metal made here now is superior to anything ever imported.

It may seem ridiculous to ask or pay such prices. Let us consider. The alloy market constitutes the bulk of the business, and governs prices. In aluminum castings, for instance, less than 2 percent of magnesium cleans up the aluminum and leaves $\frac{3}{4}$ to $1\frac{1}{2}$ percent in the casting, about doubling its tensile strength, and quadrupling its resistance to shock or jar. It reduces the cost of machining more than 50 percent, halving the number of resets on the cutting tool, giving clean-cut machine surfaces, and permitting a polish to be secured with the last cut instead of a separate operation. With care, $1\frac{1}{2}$ percent of magnesium at \$5.50 per lb. is all that is needed, *i. e.*, 8 $\frac{1}{4}$ c. per lb. of casting actually required to do the same work. The increase in strength means, in some cases, a reduction in weight of casting of 50 percent

and generally not less than 25 percent. The saving in machine work alone when the casting is to require much machine work more than pays for the use of magnesium.

So much for the consumer or user. Now the manufacturer of magnesium has at present certain considerations (of necessity rather than mere excuse) for the high prices. Cost of production abroad prior to the war approximated \$1.00 per lb. Sales in England were about \$1.30 and here about \$1.45 per lb. At that time $MgCl_2 \cdot 6H_2O$ was selling for about \$18 per ton. Present prices here are now about \$60. Other chemicals used in the manufacture have increased to ten times their normal price. One other factor, *i. e.*, insurance, must be considered in two forms: First, the insurance against cut prices and dumping that may come immediately upon the close of the war, making the plant and market-development work absolutely worthless. Second, the insurance against partisan interference. As a matter of fact in the case of two plants not a pound of material from either of which has gone for foreign military purposes so far as we know, there have been repeated efforts at molestation and some serious interruptions.

In considering prices it is well to mention separately export prices. Before the war nearly all the magnesium for England, as well as the U. S. and France, came from Germany. Since the war both France and England are producing in considerable quantities of excellent purity. This fact and the failure abroad to realize the strenuous conditions here, account for the unwillingness of buyers abroad to pay more than \$3.50 for powdered metal (all the above-named prices were ingot or bar).

At present there is being produced here at two points about all the present alloy market will absorb, and an increase of plant is being made of about 25 percent the present capacity. One other producer makes only about his own requirements. Two others are soliciting business but have failed to fill orders—in one case the order is not over a year old and still stands unfilled. All told, we believe the present production is at the rate of something over \$1,000,000 a year and will be slightly in excess of the present domestic needs.

The use of the metal for scavenging purposes depends on price of metal compared with price of material to be scavenged. For use with copper, brass, bronze, etc., the magnesium can be used at far higher prices than for steel. But the big consumption of the material can come only when it directly replaces aluminum as the predominant metal in the alloy, and arrives at a correspondingly low price. It makes beautiful castings, machines easily and well, is about a third lighter than aluminum and can be made about two to four times as strong. The coefficient of expansion reported is practically the same as for aluminum. When properly pure (over 99.5 percent) it is apparently quite as resistant to corrosion as alumi-

num, equal if not superior in electrical conductivity (about half that of copper) and superior in heat conductivity to aluminum (also about half that of copper).

1. Reduction of fused MgCl_2 with sodium involves the production of metallic sodium; we have been using the Castner process for this purpose to satisfy ourselves just what the sodium would cost and what the possibilities in this direction were. Existing conditions, the demand for sodium and sodium peroxide, forbid its consideration with a minimum of about 2 lbs. of sodium consumed for every pound of magnesium produced, and the necessity of producing dehydrated fused MgCl_2 to start with.

2. Electrolysis of the fused double chloride (usually $\text{MgCl}_2 \cdot 2\text{KCl}$) has been perfected and is very largely used abroad. We have commercially used and studied the process here and, with the cheapest water power and chloride, prices even under normal conditions by this process *must* rule above \$1.00.

3. Reduction with carbon (patented) is absolutely fascinating in its possibilities. The product is a black or gray powder. Believing such a product would be valuable, the manufacture was carried out on a scale of about 25 lbs. per hour. As the difficulty of selling the product became apparent, much time and effort were devoted to attempts to recover the metal in fairly pure form. Owing to serious objection both on the side of cost and regularity of product this process was superseded.

The other processes—electrolysis of dissolved MgO ,¹ reduction of fused MgCl_2 with aluminum,¹ reduction of oxide or carbonate to slag-forming residues,¹ etc.—will be discussed on some other occasion when the engineering problems they involve are believed to be finally solved in the best way and the patent office has finished considering them. The chemical side of each has been thoroughly worked out, however, so that some conclusions may be drawn from the large laboratory or small commercial operations. These may be of considerable interest.

At least one of the processes appears to be adapted to produce directly metal averaging 99.6 percent purity in tons per day instead of pounds. Laboratory tests give a raw material cost of 4c per lb. of magnesium and indicate a fuel cost which approaches 3c as a theoretical limit, though the practical figure will probably be several times as high. The final selection of various possible engineering means and methods remains to be worked out, but it scarcely seems possible that either labor or repairs should exceed 2c per lb. Thus if commercial yields maintain the experimental level and three times the theoretical power is commercially required, we have prospects of a net factory operation cost (without interest, amortization, insurance, patent, administration or selling) of 17c per lb. If only 75 percent yield is obtained this net

factory cost would be about 22c or a total cost with all overhead expenses of 35c and a selling price of 40c to 50c according to tonnage.

It may be asked with perfect propriety, "Why talk about it now? Some fool will certainly want you to make a contract with him at lower prices, possibly at 50c. He will not realize that it is only the present price of \$5.50 that justifies or even makes possible the \$1,000 to \$10,000 experiments that have been tried and must be tried again and perhaps again during the next three to five years before the tide turns. You will be pestered for years with this 17c talk." We have carefully considered this probability. The men who are doing this work do not cultivate talkativeness as a preference. Just at this time, however, certain consideration of public welfare should take precedence of preference. National self-preservation demands the subordination of personal interest. If we expect representatives at Washington to jettison the pork barrel, the army post, the high tide navy yard, and political trading generally, and give us a fighting chance for our lives in the scrap that is certainly coming, we must set the example of considering national interest first. If we are to have the army and navy preparedness for which we have already wasted more money than Germany has paid for her wonderfully efficient fighting machine, if we are to have any preparedness instead of repairs or regrets, we must co-operate with all we have in service, information and suggestion.

Therefore, at the risk of criticism and possible financial sacrifice it seems to be a duty at this time to point out what may possibly be expected of magnesium. Few realize the extent to which it is valuable in military work. One of the great foreign explosive experts stated that he would be glad to pay \$1.50 per pound for 500 tons. A single contract for shrapnel being executed in this country would require about 50 tons. The illuminating bombs to make daylight over the enemies' works and trenches consume large quantities. The trailers attached to shells serve at night to show the effectiveness of the fire. For all these purposes magnesium produces a result that cannot be approached by antimony or aluminum. But consider what it means to aeroplane, dirigible, and motor construction, to highspeed engines of every type, to reduce weight one-third and double strength. This material has a density of 1.75 and may be hot-rolled to a tensile strength of 35,000 lbs. per sq. in. or cold-rolled very much higher. Although five or six men are being kept practically all their time on the development of these possibilities, the broad, quick development is a task for the energy of hundreds, even thousands. Feeling the responsibility which the knowledge of the possibilities entails, it became the duty of those in charge of this work to let others know and be active in their side of preparation—the application of the material.

¹Patent applied for.



ANALYSIS OF ONE-BATH CHROME LIQUORS.*

Chrome Determination.—Dilute a measured quantity of the liquor with water to a definite volume so that the dilution contains from 0.15 to 0.25 percent of Cr_2O_3 . To 10 cc. of this dilution in a 300 cc. Erlenmeyer flask add about 50 cc. of water and about 2 grams of sodium peroxide. Boil gently thirty minutes, adding water if necessary to keep the volume from falling below about 15 cc. Cool, neutralize with strong HCl and add 5 cc. excess. Cool again. Add 10 cc. of a 10 percent solution of potassium iodide. After one minute run in from a burette 0.1 N sodium thiosulphate until the iodine color has nearly disappeared; then add a few cc. of starch solution (1 gram per liter) and titrate to the disappearance of the blue. One cc. of 0.1 N thiosulphate is equivalent to 0.002533 gram Cr_2O_3 .

Acid Determination.—Place 50 cc. of the above dilution in a 7-inch porcelain dish, add about 400 cc. of water and 1 cc. of a 5 percent solution of phenolphthalein and bring to a boil. While boiling, titrate with 0.5 N NaOH until the pink color persists after one minute boiling. One cc. 0.5 N NaOH is equivalent to 0.02002 gram SO_3 , 0.02452 gram H_2SO_4 , 0.01773 gram Cl or 0.01823 gram HCl.

Basicity.—The basicity is the ratio of basic radical to acid radical, found by dividing the percentage of Cr_2O_3 by the percentage of SO_3 or of Cl, carrying the quotient to two decimal places.

ANALYSIS OF CHROME LEATHER.

Chrome Determination.—(a) Ash 3 grams of leather. Mix the ash well with 4 grams of a mixture of equal parts of sodium carbonate, potassium carbonate and powdered borax glass and fuse for 30 minutes. Dissolve the cooled fusion in hot water with enough HCl to make the solution acid. Filter. If there is any residue on the filter, ash it and treat the ash with 1 gram of the fusion mixture in the same manner as the original ash, adding the solution to the first. Make up to 500 cc. To 100 cc. of this solution in an Erlenmeyer flask, add 5 cc. HCl and proceed as above.

(b) If it is not desired to determine Fe or Al, the ash of 3 grams of leather may be transferred to an iron crucible, mixed with 3 grams of sodium peroxide and fused 10 minutes. Place cooled crucible in 300 cc. water in a casserole and boil 20 minutes. Wash

into a 500 cc. flask, cool and make up to the mark. Filter through a dry filter. Place 100 cc. of filtrate in Erlenmeyer, neutralize with HCl, add 5 cc. excess and proceed as above.

ANALYSIS OF LACTIC ACID.

Free Sulphuric Acid.—Dissolve 50 grams of the sample in 200 cc. alcohol, which should be neutral, and of at least 95 per cent strength. Heat to 60° C., cover and let stand over night in a warm place. Filter off precipitated material and wash with alcohol. Evaporate off the alcohol, make up residue to 250 cc. with water, add 5 cc. strong HCl, boil, add BaCl_2 and determine BaSO_4 in the usual way. Calculate to per cent H_2SO_4 on the original sample.

Volatile Acid.—Weigh out 1 gram of sample, make up to about 50 cc. with water, titrate with 0.5 N NaOH. Calculate the result to lactic acid: (1 cc. 0.5 N NaOH = 0.045 gram lactic acid.) On this basis, make up a solution containing about 15 grams of acid per liter. Place 150 cc. of this dilution in a long-necked 300 cc. Kjeldahl flask, connected through a Kjeldahl bulb trap to a vertical spiral condenser, the total height from the bottom of the flask to the top of the turn connecting with the condenser being between 20 and 24 inches. Distill over 125 cc. in from 47 to 53 minutes, counting from the time the first drop falls into the receiver, which should be a graduated cylinder. Add 125 cc. of water to the residue in the flask and repeat. Titrate both distillates with 0.1 N NaOH and phenolphthalein and calculate result to grams of acetic acid: 1 cc. 0.1 N NaOH = 0.006 gram acetic acid. From these figures for acid found in distillates find actual weight of volatile acid placed in boiling flask, by means of table, and calculate this result to percentage of volatile acid in the sample.

Free Acid and Anhydride.—Titrate 50 cc. of the dilution made up for volatile acid, in the cold, with 0.5 N NaOH and phenolphthalein to first full pink. Call this figure "first titration." From it subtract a number of cc. of 0.5 N NaOH equivalent to the sum of volatile acid and free sulphuric acid present in the 50 cc. of dilution. (If the sample contains free oxalic or hydrochloric acid, the amount must be determined by appropriate methods, and further deduction made.) Calculate the remainder to lactic acid and express it as a percentage of the sample. This is the free lactic acid. After completing the first titration, add 4 cc. excess alkali, or in the case of concentrated acids 5 cc., and stand aside at room temperature (20-25° C.), for 15 minutes. Then add 5 cc. 0.5 N H_2SO_4 , boil,

*From the Journal of American Leather Chemists' Association.

and titrate back with 0.5 N NaOH. The amount of alkali used by anhydride is now found by subtraction and calculated to lactic acid. Express this as per cent of lactic acid equivalent to anhydride present in sample.

AN ANALYSIS OF OIL-GAS TAR.*

By H. E. BRUNKOW.

The recent sudden demand for benzene and other light oils found in coal tar, has led men everywhere to develop old sources of supply and to seek new ones. One of the most likely products to look to seems to be oil-gas tar. The writer having made a series of practical analyses of this tar, endeavors to set forth the methods used and results obtained, and hopes that contemporary experimenters may profit by this knowledge.

The tar used was the by-product of a gas averaging 570 B. T. U. and therefore generated at a higher temperature than is ordinarily used, made from a California crude with a gravity of about 18.8° B. The tar was pumped from the separator through a series of screens, to a settling tank, and from there to a storage tank from which the test samples were taken. The specific gravity of the tar at 95° F. was 1.026.

The first process of a logical investigation of a tar is distillation with condensation of the fractions. But in this product a difficulty was encountered, in that the tar could not distill without frothing or bubbling over. Also naphthalene clogged the condenser tube after heating a short time.

To overcome the latter difficulty, picric acid was introduced into the still with the tar, to precipitate the naphthalene; but the frothing over still continued, in spite of the fact that the greatest precautions were used in heating. In one instance the temperature in the electrically heated still was raised only a few degrees each hour over a period of several days. These facts led to the conclusions that: (1) the tar contained an extraordinary amount of water; (2) the naphthalene deposited because of the absence of solvent light oils.

Several other methods were tried to determine the quantity of water. One of these, the calcium carbide method (Proceedings, Pacific Coast Gas Association, vol. 8, p. 458), gave satisfactory results, but necessitated an elaborate apparatus. Another method was distillation under a vacuum of 17' mercury. This was successful, in that it eliminated to a great extent the condensation of naphthalene in the condenser tube, and also required only low temperatures. Still another method was to place a sample in a drying oven for twenty-four hours at 212°F. This was not tried until it was certain that no large quantity of light oils was present.

The next step was to determine the soluble oils and

lampblack. For this an ordinary Soxhlet extraction apparatus was used, with carbon-disulphide as the extracting liquid. After the process was completed, the tarred extraction thimble with the lampblack was dried and weighed, as was also the flask containing the oils.

The naphthalene was determined by placing a sample of tar in a silica boat, and putting this in a glass tube connected directly to a Drechsel's gas washing bottle, with another bottle in series, both containing standardized picric acid solution. The last bottle was connected to a filter pump and air drawn through, which, passing over the tar sample, carried the gas naphthalene with it. The tube was gradually heated so that all the naphthalene was expelled from the tar.

The results obtained were as follows:

Sample.	Water.	Method.	Lamp-black.	Heavy Oils.	Naphthalene.
(1)....	64.4%	Cal. Carbide			
(2)....	65.6%	"			
(3)....	60.0%	Distillation	8.6%	25.1%	
(4)....	60.9%	"			
(5)....	60.7%	Evaporation	10.8%	27.1%	
(6)....					4.5%

In the distillation, a small quantity of naphthalene came over with the water, as did also a little light oil—less than 0.2%—the nature of which was not determined. The lampblack contained a small amount of salt which was also disregarded. The heavy oil, after drying at 212° F. and cooling, became hard, and was assumed to be asphaltum.

Averaging the above percentages we have:

Water	62.3%
Lampblack	9.7%
Asphaltum	26.1%
Naphthalene	4.5%
Total	101.9%

The conclusions derived from these results are as follows:

(1) The bulk of the water is held in an emulsion. The lampblack, which is throughout in the tar, is also saturated with water. Both these conditions are causes for frothing, and so under no ordinary conditions can this product be successfully distilled.

(2) The tar is saturated with naphthalene, as is evidenced when a sample is kept in a container. After a short time crystals deposit on the sides with the slightest cooling.

(3) The only reason the tar can be successfully pumped is because it contains a high percentage of water. This is also reason why it can be readily burned under a boiler, the water making it easy for the steam to atomize the emulsion.

(4) The tar is worthless for the recovery of valuable light oils.

The exports of kauri gum to the United States during 1915, according to invoices certified at the American consulate general at Auckland, New Zealand, were valued at \$1,087,601, against \$1,501,375 worth for 1914.

*From Journal of Electricity Power and Gas.

THE CONSTITUENTS OF LICORICE ROOT AND OF LICORICE EXTRACT.*

PART 2.

By PERCY A. HOUSEMAN,† Ph.D., F.I.C.

Since the appearance of Part 1¹ of this paper I have carried out a considerable amount of work on licorice, aiming at the improvement of the method of analysis, but have not seen fit to make any decided changes in the method previously given by me. The separation of the glycyrrhizin from the starch and gums is now effected with 75 per cent alcohol, as it was found that 80 per cent alcohol precipitated, in some cases, a small quantity of glycyrrhizin. The crude glycyrrhizin is still determined by precipitation with dilute sulphuric acid, no other method having been found practicable. The method for sugars remains unaltered, and gives reliable results.

Partly because of the imperfections in the methods of analysis, and partly because of the large fluctuations in the composition of pure licorice root and extract, chemical standards of purity have not yet been established for these materials.

In Part 1 there was discussed the behavior of various solvents toward licorice root from different localities. The quantitative differences found were much less marked than might have been expected, considering the marked differences of flavor of the various roots and extracts. These differences of flavor are possibly to be ascribed to the nature, rather than to the amount, of the flavored constituents.

A summary is here made of the results of some recent extractions of licorice root with ether, 99 per cent alcohol, 75 per cent (by volume) alcohol, 50 per cent (by volume) alcohol, and water (see Tables I, II, and III).

A comparison of these results with those given in Part 1 shows:

1. *Ethereal extracts* range from 2.9 per cent to 4.9 per cent (Table I) and agree fairly with those of Part 1.

2. *Alcoholic Extracts*.—99 per cent alcohol extracts 4.8 per cent to 7.0 per cent (Table II), whereas 95 per cent alcohol, which was used in Part 1, extracted 10.8 to 12.7 per cent. The figures obtained with 99 per cent alcohol give results which correspond more nearly to the true amount of total resins present than do those previously obtained with 95 per cent alcohol, since the latter extracts from licorice root other materials besides resins, notably cane-sugar, as was shown in the detailed analysis of these extracts (Table IX, Part 1).

It is to be noted that R. Kobert,² in an article concerned chiefly with the saponins of licorice root, reproduces Table VIII from my previous paper. He changes the heading of column 1 of that table to

"Ether-soluble resins," and the heading of column 2 to "Ether-insoluble resins"; but the latter designation is incorrect, for the reason just stated above. B. Müller,³ in a translated summary of Kobert's article, also reproduces the same table, but has omitted to state that it is from my paper in this Journal. The inference from the text of the translation is that the table is the work of Tschirch.

The 50 per cent alcohol extracts (Table 1) compare well with those published in Part 1 of this paper.

In the new results the same feature is observed as was noted in Part 1, viz., the different roots show smaller differences in the amounts extracted by the respective solvents than would be expected.

PREPARATION OF CANE-SUGAR FROM LICORICE ROOT.

Rasenack⁴ appears to have been the only worker who actually obtained and identified crystals of cane-sugar from licorice root. He observed a deposition of crystals of cane-sugar from an alcoholic extract of licorice root.

I have worked out a systematic preparation of cane-sugar from the root as follows:

Russian licorice root was ground, and macerated with cold 5 per cent (by weight) sulphuric acid. Three liquors were taken off, pressing the root between each extraction. The liquors were united, centrifuged, exactly neutralized with sodium hydrate, brought to a boil, and filtered from albuminoids. The filtrate was evaporated *in vacuo* to small volume, and treated with about six times its volume of 95 per cent alcohol, so

TABLES I, II AND III—SUBSTANCES DISSOLVED FROM LICORICE ROOT BY VARIOUS SOLVENTS.

(The solvents were used in the order given below.)

	Anatolian.	Russian.	Syrian.	Turkish-Arabian.	Spanish (Toledo).	Italian.
Table I—						
Root moisture	4.0	4.0	4.5	3.0	3.5	4.5
Ether	3.6	3.6	4.9	3.7	2.9	3.6
99 per cent alcohol	2.0	2.2	2.1	2.1	2.0	1.6
50 per cent alcohol	28.2	25.9	23.0	20.5	22.6	25.0
Hot water	5.5	1.7	3.9	3.9	6.4	8.2
Spent root	56.7	59.6	61.6	66.8	62.6	57.1
	100.0	100.0	100.0	100.0	100.0	100.0
Table II—						
Root moisture	2.2	2.5	2.2	2.2	2.0	2.1
99 per cent alcohol	5.5	5.6	7.0	5.4	4.9	4.8
75 per cent alcohol	23.3	22.2	19.1	16.9	19.7	21.2
Hot water	10.9	10.6	8.2	8.9	9.9	12.2
Spent root	58.1	59.7	63.5	66.6	63.5	59.7
	100.0	100.0	100.0	100.0	100.0	100.0
Table III—						
Root moisture	6.5	7.5	8.0	7.0	7.0	8.0
Hot water	37.1	35.7	31.8	29.6	33.3	36.3
75 per cent alcohol	1.0	3.5	4.1	3.4	2.8	3.4
Spent root	52.1	53.3	56.1	60.0	56.9	52.3
	100.0	100.0	100.0	100.0	100.0	100.0

*American Journal of Pharmacy (Vol. 87), No. 12, pp. 555-559.
B. Müller's translation of Kobert's article contains the following errata:

On p. 557, instead of $C_{41}H_{64}O_{16}$ read $C_{41}H_{64}O_{16}$.
On p. 558, instead of glycyrrhetic acid read glycyrrhetic acid.

On p. 558, instead of glycyrrhizic acid read glycyrrhizic acid.
*Arbeiten aus dem Kaiserlichen Gesundheitsamte, 1908, vol. 28, p. 412.

*From American Journal of Pharmacy.

†Laboratory of MacAndrew & Forbes Co., Camden, N. J.

1 American Journal of Pharmacy, 1912 (Vol. 84), No. 12, pp. 521-546.

2 Berichte der Deutschen Pharmazeut. Gesellschaft, 1915, Heft 4, pp. 169-185.

that the mixture contained about 85 per cent alcohol. The starch and gummy matters, together with precipitated sodium sulphate, were removed by filtration, and the clear brown solution again evaporated *in vacuo* to small volume. The liquid was then boiled for half an hour with a concentrated aqueous solution of strontium hydrate, allowing three parts of strontium hydrate to every one part of cane-sugar supposed to be present. The precipitated strontium sucrate was filtered hot and boiled a second time with strontium hydrate solution. The strontium in the precipitate was now removed by suspending in water and passing in carbonic acid gas. The light yellow filtrate was evaporated to a syrup, and repeatedly crystallized from boiling 95 percent alcohol.

The identity of the substance as cane-sugar was established by its crystalline form, by its specific rotatory power $[\alpha]_D = 66.3^\circ$, and by analysis.

	Calculated.	Found.
Carbon	42.07	42.00
Hydrogen	6.52	6.43
Oxygen	51.41	51.57
	100.00	100.00

The yield of cane-sugar was about 2 percent of the root used.

DETECTION OF SAPONINS IN LICORICE ROOT.

At the time my experimental work was carried out on saponins in licorice root (1914) nothing had been published on this subject. The presence of saponins in licorice root was rendered probable by a number of properties of the extract.

The hæmolysis test was used for the detection of biologically active saponins. The method employed was to obtain the supposed saponin in aqueous solution and mix it with salt solution, so as to produce a liquid containing 0.9 percent sodium chloride, and then add a suspension, in physiological salt solution, of the washed corpuscles of sheeps or ox-blood. Solution of the blood corpuscles shows the presence of a saponin of sapogenin, or both.

Negative results were obtained with aqueous extracts of both green and dried licorice root. Mild and strong extractions were tried, but no hæmolysis was observed at any concentration.

Negative results were also obtained with extracts in which dilute alcohol up to a strength of 50 per cent (by volume) was employed as a solvent.

Hæmolytically active saponins were extracted from both green and dried licorice root by 75 per cent (by volume) alcohol. The 75 per cent alcoholic extract was evaporated to dryness, the residue extracted with cold water, and tested with washed blood corpuscles in the usual manner. The limit of dilution for complete solution of the blood corpuscles at room temperature was approximately 1 part of licorice root to 640 parts solution. In the particular samples tested, Syrian, Spanish and Italian roots possessed the strongest hæmolytic power, and were followed by Russian, Anatolian and Turkish-Arabian. It is likely that this order might be changed if a different set of sam-

ples of root were tested. I found, further, that the biologically active saponins of licorice root are in the *inner* bark, and are not contained in the outer bark, nor in the central part of the root. Comparative tests with soap bark gave complete hæmolysis at a dilution of 1 to 2,000 at 20°C .

R. Kobert⁵ states that the sapogenin, glycyrrhetic acid, which is probably present in small amount in licorice root, is responsible for the hæmolitic activity of extracts from the root. It is, however, probable that glycyrrhetic acid would not be obtained in solution by the treatment of a 5 per cent alcohol extract with cold water. Moreover, glycyrrhetic acid is insoluble in ether, and ethereal extracts of licorice root contain hæmolytically active material. It seems likely, therefore, that licorice root contains an active saponin as well as a sapogenin. Kobert has given particular attention to the relation of glycyrrhizic acid to the saponins, and to the relation which Tschirch's formula, $\text{C}_{44}\text{H}_{84}\text{O}_{19}$, for glycyrrhizic acid bears to that of the general formula $\text{C}_n\text{H}_{2n-5}\text{O}_{10}$, which Kobert has established for saponins. Sormanni⁶ found glycyrrhizic acid to be hæmolytically inactive. Kobert confirms this, and finds, further, that glycyrrhizic acid yields an active sapogenin (glycyrrhetic acid) on hydrolysis with dilute sulphuric acid. Both of these statements I have confirmed. Kobert concludes that glycyrrhizic acid is a member of the group of inactive saponins.

PREPARATION OF GLYCYRRHIZIN (GLYCYRRHIZIC ACID) FROM LICORICE ROOT.

Tschirch and Cederberg⁷ have described the preparation of pure glycyrrhizin from licorice root. They precipitated an aqueous extract of the root with dilute sulphuric acid, and purified this crude glycyrrhizin by the preparation of the tertiary and primary potassium salts, passing to the free acid by means of the decomposition of the lead salt with sulphuretted hydrogen. The primary potassium salt and the free acid were purified by repeated crystallization from hot glacial acetic acid.

In preparing glycyrrhizin, I first extracted decorticated licorice root about six times with 95 per cent alcohol in order to remove resinous and bitter principles. The glycyrrhizin was then removed from the residual root with 30 per cent alcohol, and was precipitated with dilute sulphuric acid after removal of the alcohol. It was thought that this would give a crude glycyrrhizin which would be more readily purified than that obtained by Tschirch's method of extracting the original root with water and precipitating with dilute sulphuric acid, since by this latter method a larger number of other constituents are mixed with the glycyrrhizin, and must be later separated.

The crude glycyrrhizin from 30 pounds of root was washed twenty times by kneading with warm water, and was treated with alcohol and ether as prescribed by Tschirch. The precipitates obtained from the ad-

⁵Loc. cit.

⁶Zeit. f. Nahrungs- und Genussmittel, 1912, 23, p. 56.

⁷Archiv der Pharmazie, 1907, Heft 2, p. 97.

dation of alcohol and ether were insignificant. The yield of tertiary potassium salt was 5.7 per cent of the root. The tertiary potassium salt was converted to the primary potassium salt by means of hot glacial acetic acid. The primary salt was crystallized twice more from glacial acetic acid, and washed with the same solvent. A white product was obtained. The primary potassium salt was converted to the lead salt by dissolving it in warm dilute (1:4) alcohol and precipitating with basic lead acetate. The lead salt was converted to the free glycyrrhizic acid by means of sulphuretted hydrogen, according to the directions given by Tschirch. The solution of the glycyrrhizic acid was evaporated to dryness *in vacuo*, and crystallized twice from hot glacial acetic acid.

The following combustion figures were obtained after the glycyrrhizic acid had been allowed to stand over potash in a vacuum desiccator:

0.2914 g. substance gave 0.6262 g. carbon dioxide and 0.2028 g. water.	
0.3050 g. substance gave 0.6512 g. carbon dioxide and 0.2110 g. water.	
0.2978 g. substance gave 0.6344 g. carbon dioxide and 0.2010 g. water.	
0.2976 g. substance gave 0.6381 g. carbon dioxide and 0.2066 g. water.	
0.3000 g. substance gave 2.8 cc. nitrogen at 26° C. and 768 mm. pressure.	
0.3000 g. substance gave 3.0 cc. nitrogen at 23° C. and 768 mm. pressure.	

A portion of the glycyrrhizic acid upon which the above combustions were carried out was crystallized three times more from hot glacial acetic acid. Perfectly colorless crystals were obtained. This purified glycyrrhizic acid was then crystallized from 50 per cent alcohol, from which it did not crystallize well.

Two nitrogen estimations were carried out on this product.

	C Per cent.	H Per cent.	N Per cent.
Found { 1	58.62	7.80	1.05
2	58.25	7.75	1.14
3	58.11	7.57	
4	58.52	7.78	
Average	58.37	7.72	1.09

Calculated for $C_{18}H_{26}O_{16}$	58.90	7.19	
Calculated for $C_{18}H_{24}O_{16}$	58.64	7.61	
Calculated for $C_{18}H_{22}O_{16}$	58.51	7.81	
Calculated for $C_{18}H_{20}O_{16}$	57.81	7.39	1.53
Calculated for $C_{18}H_{18}NO_{16}$	58.97	7.31	1.56
Calculated for $C_{18}H_{16}NO_{16}$	58.77	7.63	1.55
0.3028 g. substance gave 5.12 cc. nitrogen at 26° C. and 766 mm. pressure.			
0.2748 g. substance gave 4.51 cc. nitrogen at 22° C. and 769 mm. pressure.			

Nitrogen = 1.89 per cent, 1.89 per cent.

It is not intended to controvert here the finding by Tschirch, that glycyrrhizic acid contains no nitrogen. Tschirch has been confirmed in his work by Rasenack. It is, however, very remarkable that this substance, if free from nitrogen, should so tenaciously hold a nitrogenous impurity, in spite of the elaborate purification outlined above.

The glycyrrhizic acid, prepared as above described, became brown at 185° C., and partly melted, with frothing, at 203° to 205° C. It readily dissolved in warm water, and gelatinized on cooling.

Its behavior toward sulphuric acid and toward

bromine is different from that of glycyrrhizin which has not been crystallized from acetic acid. A drop of twice normal sulphuric acid added to 1 cc. of a moderately strong aqueous solution of the purified glycyrrhizin produced no immediate precipitate. After some time the liquid became opalescent, but cleared on warming, and on subsequent cooling a granular precipitate was deposited, which redissolved on warming. Glycyrrhizin which has not been purified by crystallization from acetic acid is precipitated even by very dilute sulphuric acid, and the precipitate does not redissolve on warming. Pure glycyrrhizic acid absorbs bromine in the cold, but gives no precipitate. Impure glycyrrhizin or an aqueous solution of licorice extract gives an immediate precipitate with bromine, even in very dilute solution. The precipitate contains all of the glycyrrhizin, and is not dissolved on warming.

It is not clear why the glycyrrhizin purified with acetic acid should behave differently from crude glycyrrhizin toward bromine and toward sulphuric acid unless glycyrrhizic acid, being relatively sensitive towards decomposition, has possibly suffered some change by the action of hot glacial acetic acid.

OXIDATION OF GLYCYRRHIZIC ACID WITH POTASSIUM PERMANGANATE.

One gram glycyrrhizic acid was dissolved in a solution of 1 gram potassium hydroxide in 50 cc. water, and 3 grams potassium permanganate in 60 cc. water were added. After heating on the water-bath for 1 hour, the permanganate was decolorized. A further 1-gram permanganate in 20 cc. water provided an excess. Added 2 cc. alcohol (until the purple color was just destroyed). Filtered, and neutralized with dilute hydrochloric acid. The white flocculent precipitate (0.2 gram) was practically tasteless, and will be further investigated.

OXIDATION OF GLYCYRRHIZIC ACID WITH NITRIC ACID.

One gram glycyrrhizic acid was treated with 10 cc. fuming nitric acid. Brisk action occurred, with the development of heat and evolution of nitrous fumes. The blood-red solution was poured into water. The light yellow precipitate was very bitter, and was readily soluble in alcohol and in ammonia. The filtrate contained oxalic acid, and also a substance which dyes animal fibres a fast yellow. The solution of this dye has a very bitter taste, but does not contain picric acid.

The resins (soluble in ether) and the bitter principles (soluble in alcohol, insoluble in ether) of licorice root both show behavior toward nitric acid similar to that shown by glycyrrhizic acid.

ISOLATION OF A YELLOW DYE FROM LICORICE ROOT.

A piece of silk dipped in an aqueous licorice extract is dyed a pale but fast yellow. The dye is obtained by percolating licorice root with hot water, evaporating the solution to dryness, and extracting with absolute alcohol. The alcoholic solution is evaporated to dryness, and the dye extracted with hot water. The dye is not picric acid.

DETERMINATION OF BARIUM CARBONATE AND BARIUM SULPHATE IN VULCANIZED RUBBER GOODS.

In a recently issued Bureau of Standards Technologic Paper (No. 64), a new method is given for the determination of barium carbonate in vulcanized rubber goods. This paper was prepared by John B. Tuttle, associate chemist of the bureau. The paper follows:

With the advent of buying rubber goods on specifications it became necessary to develop methods which would accurately determine the various constituents. One of the most important determinations is that of total sulphur. In a recent publication of the bureau¹ the sulphur-bearing constituents of vulcanized rubber goods were mentioned, and a method was given for a quantitative determination of the sulphur which they contain. In this article it was stated that sulphur may occur in various forms including metallic sulphates, usually lead and barium. Many specifications now permit the use of barium sulphate (barytes) without having the sulphur which it contains count as part of the specified total sulphur. It is therefore necessary to be able to determine the percentage of this mineral. This was not at all difficult as long as the rubber compounds contained barium only in the form of the sulphate. When, however, manufacturers began using the carbonate as well as the sulphate the problem became much more complex, since it became necessary to determine both salts of barium in the presence of each other, as well as in the presence of other sulphur-bearing minerals. It is with this phase of the problem that the present article deals.

The separation of barium carbonate from barium sulphate in the absence of other minerals is readily accomplished by solution of the carbonate in acids, such as hydrochloric, acetic, etc. In rubber compounds, however, this method is not applicable, since lead sulphate may be present, in which case part of the lead sulphate will also be dissolved, and the reaction between the lead sulphate in solution and the barium will cause the precipitation of barium sulphate, and the results obtained will be low. Lead sulphate may be dissolved in ammonium acetate, and it was thought that this disturbing constituent could be eliminated by this procedure, which, however, was found to be too slow and unreliable to be an acceptable method. However, still another procedure is available, viz., transforming the lead sulphate to the carbonate by boiling with alkaline carbonates, and filtering off the soluble sulphates. Sodium carbonate readily converts lead sulphate and barium sulphate² into their carbonates; ammonium carbonate reacts

with lead sulphate, but tests made here show that it has only a slight effect on barium sulphate. By treatment with ammonium carbonate, we can therefore change the lead sulphate into the carbonate, and then filter the soluble sulphates from the lead carbonate, barium carbonate, and barium sulphate. Calcium and zinc carbonates, which may be present, do not interfere with the desired separation.

The four samples used in this investigation were of known composition, having been compounded and vulcanized at this bureau. Their composition was as follows:

TABLE I.—COMPOSITION OF SAMPLES.

	Compound No. 1. Per cent.	Compound No. 13. Per cent.	Compound No. 16. Per cent.	Compound No. 17. Per cent.
Fine Para rubber ..	39.6	30.0	20.0	
Plantation rubber ..				40.0
Sulphur	2.5	3.0	2.0	4.0
Litharge	8.6	7.0	8.0	8.0
Zinc oxide	8.7	20.0	20.0	15.0
Sublimed white lead ..	30.6			
Barium carbonate ..	10.0			10.0
Barium sulphate ..		20.0	30.0	20.0
Whiting		20.0	20.0	
Vaseline				3.0
	100.0	100.0	100.0	100.0

The barium carbonate used in No. 1 and No. 17 was Merck's best quality, and was finely ground before compounding. The barium sulphate was tested and found to contain practically no soluble barium salts. It will be noted that No. 1 contained both barium carbonate and lead sulphate; No. 17 barium carbonate and barium sulphate; while No. 13 and 16 contained barium sulphate only.

Schaeffer³ has shown that the organic matter in rubber can be removed by ignition in an atmosphere of carbon dioxide without change of sulphur to sulphide, or of either to sulphate. Slight reduction of barium sulphate to sulphide may occur during ignition of the rubber, but experience shows that the amount of sulphide formed is practically negligible. The apparatus used for the decomposition of the rubber was practically the same as that used by Schaeffer, the only change being that the sample was placed in a porcelain boat so as to facilitate the removal of the residue from the glass tube. One gram of the rubber was taken for each determination. After ignition and cooling in carbon dioxide the boat was removed, the residue finely ground in an agate mortar, transferred to a 250 cc. beaker, and treated with 5 to 10 g. ammonium carbonate, 15 to 20 cc. of strong ammonia water, and about 50 cc. of distilled water. The mixture was boiled for 15 to 30 minutes, filtered, and the precipitate thoroughly washed to remove all soluble sulphates. The residue on the filter paper was washed back into the original beaker with distilled water, about 10 cc. of glacial acetic acid and sufficient water to make the total volume of the solution about 100 cc. were added. This was heated to boiling and then filtered through the same filter paper as before. By this procedure, lead, barium, calcium, and

¹Noyes and Bray, *J. Am. Chem. Soc.*, 29, p. 151 (1907), state that 80 per cent of barium sulphate is converted into barium carbonate when boiled with an excess of sodium carbonate.

²Bureau of Standards Technologic Paper No. 45; *J. Ind. Eng. Chem.*, 7, p. 658 (1915).

³*J. Ind. Eng. Chem.*, 4, p. 837 (1912).

zinc carbonates pass into solution, while barium sulphate and lead sulphide are not attacked. Hydrogen sulphide was passed into the filtrate, the lead sulphide filtered off, the filtrate heated on the steam bath, and 10 cc. of 10 percent sulphuric acid added. The solution was allowed to stand overnight on the steam bath; the next day the precipitate was filtered off, ignited in a porcelain crucible, cooled, and weighed.

TABLE II.—RESULTS OF BARIUM CARBONATE DETERMINATION.

All results are expressed in percentages of the original sample.					
Sample.	Constituents.	Present.	Found—		
1...	Barium carbonate	10.0	9.72	9.67	9.98 10.02
	Sulphur equivalent to BaCO ₃	1.63	1.58	1.57	1.62 1.63
17...	Barium carbonate	10.0	10.28	9.76	10.73 10.71
	Sulphur equivalent to BaCO ₃	1.63	1.67	1.59	1.74 1.74
13...	Barium carbonate	0.0	0.17	0.08	0.17 0.25
	Sulphur equivalent to BaCO ₃	0.0	0.03	0.01	0.03 0.03
16...	Barium carbonate	0.0	0.29	0.19	0.31 0.09
	Sulphur equivalent to BaCO ₃	0.0	0.05	0.03	0.05 0.02

The barium sulphate was calculated to barium carbonate, using the factor 0.845. The sulphur in the barium sulphate was also calculated, since it is desirable to know just what error will be introduced if the barium present in the form of the carbonate should be considered as being present as the sulphate. The results on sample No. 1 show that in the presence of lead sulphate (in the sublimed white lead), barium carbonate can be determined with accuracy, the results, expressed in terms of sulphur, being within 0.05 percent of the calculated amount. In sample No. 17 we have present both the sulphate and carbonate of barium, and while the results are not as good as those obtained on sample No. 1, they are sufficiently accurate for all practical purposes, the maximum error on sulphur being only 0.11 per cent. Results slightly higher than those calculated must be expected, since samples Nos. 13 and 16, which contain barium sulphate and no barium carbonate, yield small amounts of precipitate by this method, partly in consequence of slight reduction of barium sulphate to sulphide during the ignition of the rubber, and partly on account of the slight action of ammonium carbonate on barium sulphate. These amounts, in themselves, are negligible. It is apparent, therefore, that neither lead sulphate nor barium sulphate interferes appreciably with the determination of barium carbonate by this procedure.

METHOD FINALLY ADOPTED.

The total barium in the rubber compound is determined as barium sulphate by the method for the determination of barytes in use at this bureau.⁴ This method was first suggested by C. E. Waters, and afterwards modified by W. H. Smith and the author. Barium carbonate is determined in a separate sample by the method just described, and an equivalent amount of barium sulphate is deducted from the total barium sulphate. The sulphur in the remaining portion of barium sulphate is calculated, and the total sulphur determination is corrected by this amount.

A SUBSTITUTE FOR SEA SAND.

By F. W. Bruckmiller.*

A few years ago the writer's attention was called to a new material to be used in the cleaning of platinum ware, which after some trial has proven quite satisfactory. The material in question is volcanic ash, the base of a number of commercial household cleansers. Analysis shows it to be nearly pure silica in a rather fine state of division. Ninety-eight per cent passed a 100-mesh sieve, while 90 per cent passed a 200-mesh sieve. The individual particles are not rough although angular, and in no way scratch the surface of the platinum. The loss in weight of a platinum crucible is no more when using it than when using sea sand. Viewed with the microscope the individual particles are very irregular in outline, but no more so than sea sand. The product costs less than sea sand and for this reason since it does the work just as good, has replaced sea sand in our laboratory. It retails for 5 cents a pound. The dealer's name can be furnished on request.

The Bureau of Chemistry of the U. S. Department of Agriculture for several years has been investigating the sanitary conditions in the production and distribution of bottled mineral and table waters, which are offered for sale in interstate commerce and therefore subject to the Food and Drugs Act. It is recognized that the sale of bottled waters is dependent largely upon the belief by the public in the purity of the product. The Bureau has recently conferred with a large number of sanitary experts and bacteriologists regarding a desirable standard for judging the sanitary character of bottled waters. As a result of the investigational work and the above mentioned conferences the Bureau believes that the tolerances established by the Public Health Service of the Treasury Department for waters served on interstate carriers is none too rigid for application to bottled waters sold in interstate commerce or imported from foreign countries. The Treasury Department standards are as follows:

1. The total number of bacteria developing on standard agar plates, incubated 24 hours at 37° C., shall not exceed 100 per cubic centimeter; provided, that the estimate shall be made from not less than two plates, showing such numbers and distribution of colonies as to indicate that the estimate is reliable and accurate.

2. Not more than one out of five 10 cc. portions of any sample examined shall show (by the method of the Public Health Service) the presence of organisms of the bacillus coli group.

*Bureau of Standards Circular No. 38, 3d ed., p. 68 (1915); India Rubber World, 51, p. 128 (1914).

*Water and Sewage Laboratory, University of Kansas, Lawrence.

The CHEMICAL ENGINEER

PUBLISHED MONTHLY by the MYRON C. CLARK
PUBLISHING CO.,

608 S. Dearborn Street, Chicago

Entered as Second Class Matter, Aug. 19, 1907, at the Post Office
at Chicago, Illinois, under Act of March 3, 1879.

Subscription—United States, Cuba and Mexico, \$2.00
Extra postage to Canada 25c a year; to foreign countries 50c a year.
Remittances may be made by check, draft or money order in favor of
THE CHEMICAL ENGINEER

All communications should be sent to THE CHEMICAL ENGINEER, 608
S. Dearborn Street, Chicago, Ill.

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Production of Manganese in 1915.

The manganese ore and metal industries continue to undergo readjustment, but the impetus given the domestic industry on account of the shortage of foreign ore has not brought forth the production that had been expected. Important exploratory work and preparations for milling have been carried out at several mines in Virginia, Tennessee, Colorado, and California, but except in the case of one mine this has not yet resulted in production. A close estimate of the production in the United States for 1915 cannot be made, but it is very doubtful that it exceeded 6,000 tons, as compared with 2,635 tons produced in 1914, according to D. F. Hewett, of the U. S. Geological Survey. The shortage of ore is indicated by the rise in domestic prices. During 1915 ore containing 50 per cent manganese and adapted to making ferromanganese has sold as high as \$22.50 per ton, which compares with \$12 per ton, the price paid a few months before the war began. The shortage in high-grade ores for use in the manufacture of flint glass and dry batteries has been keenly felt and several dry battery plants have been forced to close down. One producer in San Miguel County, Colorado, reports the sale of a small tonnage of ore containing 80 per cent manganese dioxide and less than 1 per cent iron,

at \$65 a ton f. o. b. at point of shipment. One consequence of the war has been the great change in the sources of imports into the United States. For the three years prior to 1915, India supplied slightly more than one-third the imported tonnage which averaged 309,682 tons a year, while Russia and Brazil supplied about equal parts of the remainder. During the first ten months of 1915, Brazil supplied 181,258 tons out of the total of 192,286 tons imported. The receipts from India were about one-twelfth normal and from Russia, negligible. In other words, receipts from Brazil were more than twice the average for the three preceding years and partly made up for the failure of supplies from Russia and India. The most recent information up to June, 1915, shows that although the Indian mines are being operated, the production is about one-fourth that of the preceding year. Even under normal conditions in the United States, about one-half of the supply of ferromanganese is imported and the other half is manufactured largely from imported ores. The restrictions placed by England upon the exports of ferromanganese greatly reduced the imports for the first six months of 1915, although they were normal during the next three months. For the first nine months of 1915 the imports were 40,863 tons, compared with 62,333 tons for the same period of 1914 and 90,752 tons for the same period of 1913. This shortage has forced two important steel producers, Jones & Loughlin Steel Co., of Pittsburgh, Pa., and Maryland Steel Co., Sparrows Point, Md., to devote furnaces to the manufacture of ferromanganese. This is noteworthy because most of the domestic ferromanganese has heretofore been made by two subsidiaries of the United States Steel Corporation, although several more firms have occasionally contributed. During the year the price of ferromanganese has almost steadily risen from \$70 a ton in January to \$115 a ton in December. Small lots are reported to have been sold at \$120 a ton in December. Although the activity of several mines may enable the production of 1915 to be trebled or quadrupled in 1916, there is little prospect that domestic deposits will make more important contributions of ore. Manufacturers of ferromanganese, as well as of dry batteries and flint glass, must continue to look to foreign countries for most of their ore supplies. Unless important new sources of ore are found, there is little prospect for reduction of prices of ores and ferromanganese to the average of previous years until the end of the European war. Efforts are being made to conserve during refining the manganese contained in raw pig iron, thereby reducing the amount of ferromanganese that must be added to make steel. If these efforts are successful, they will mark an important advance in steel metallurgy.

Lignite Resources of North Dakota.

Lignite underlines almost all the western part of North Dakota. It is estimated by the United States Geological Survey that the state contains the enor-

mous amount of 667,000,000,000 short tons of lignite in beds over 3 feet thick and within 1,000 feet of the surface, and it seems probable that there is workable lignite within this limits under every section of the land in the western part of the state. It is difficult to form an idea of a mass containing even 1,000,000 tons, and hence the figures given above are practically impossible of comprehension, but if the amount is put in the form of a cube a better conception of its magnitude may be obtained. The lignite of the state, if formed into one mass in the compact form in which it lies in the ground, would make a cube 5 miles long, 5 miles broad, and 5 miles high. Such a cube would cover nearly a township of land and would be almost as high as the highest mountain on the globe.

Much of the lignite, although of poor quality and at present used only in a small way, constitutes a vast fuel resource which will in time become of great value, not only to the individual citizens of the state but to the corporations that are seeking power for use in manufacturing or in transportation.—(Northern Pacific Guidebook, Geological Survey.)

Alloy Steel.

"Manufacture and Uses of Alloy Steels" is the title of Bulletin 100, just issued by the United States Bureau of Mines, Department of the Interior. Henry D. Hibbard, the author, in the introduction to the bulletin, says: "The object of this report is to give briefly information of present value relating to the manufacture and uses of the various commercial alloy steels with the hope of stimulating the demand for such steels and extending their practical use. The report is issued by the Bureau of Mines as a contribution to the increase of efficiency in the preparation and utilization of the mineral resources of the United States. A copy of this bulletin may be obtained by addressing the Director of the Bureau of Mines, Washington, D. C."

Radium, Uranium, and Vanadium in 1915.

Radium, uranium, and vanadium are closely connected in occurrence in the principal fields, Colorado and Utah, but in 1915, although the European war caused a great slump in the production of ores of radium and uranium, it caused a considerable increase in the production of ores of vanadium. According to reports for 1915 received by the United States Geological Survey and compiled by Frank L. Hess, the output was 23.4 tons of uranium oxide and 6 grams of radium contained in the carnotite ores produced, and 635 tons of vanadium contained in the carnotite ores shipped and in the chemical concentrates from the rescoelite ores. In 1914 the ores produced contained 87.2 tons uranium oxide, 22.3 grams radium, and 435 tons vanadium. The United States has much the largest known radium-bearing deposits of the world, but the market for radium is mostly in Europe, for, though Americans like to feel that they are suf-

ficiently progressive to take hold of and use to the full new discoveries, inventions, and processes, yet the European municipalities and hospitals have been buying and utilizing most of the radium produced. When the war began, therefore, causing European money to flow into other channels, the demand for radium fell off so greatly that there was practically no market for radium or uranium ores in the early part of 1915, and very little market during any part of the year. Mining of carnotite ores, except by the National Radium Institute (Inc.) under the supervision of and in co-operation with the Bureau of Mines, and except for such work as was necessary for assessment work to hold claims, was nearly stopped. The Institute mined nearly the 1,000 tons of ore contracted for from the Crucible Steel Mining & Milling Co.'s claims in Long Park, Montrose County, Colo., and obtained 70 tons of concentrates, carrying about 3 per cent of uranium oxide, by concentrating material carrying 0.7 per cent, which had been thrown on the dumps. The Institute fully accomplished its purpose to work out a practical process of producing radium at a cost much below the market price of the element and crystallized out radium salts containing 6 grams of the element. It delivered during the year 3,000 grams of radium (element) at a cost of \$37,599 per gram. Near the close of the year 1.1 grams of radium (element) was contracted for by a private company for \$132,000, or \$120,000 a gram. This comparison shows the great success of the work of the Bureau of Mines. Its ore concentration method seems to have also been highly successful. After mining its quota of ore from the Crucible Steel Mining & Milling Co.'s property, the Institute came into the market as a purchaser of ore. In the later half of the year Dr. W. A. Schlesinger and associates established a radium reduction plant in Denver. They acquired an interest in the Copper Prince claims, from which ore was mined, and bought a further quantity. Ore carrying about 5,000 pounds of uranium oxide, containing about 640 milligrams of radium, was treated during the year. The Carnotite Reduction Co., made up of Dr. H. N. McCoy of the University of Chicago and associates, purchased from Galloway and Belisle a quantity of ore which had been stored in Placerville, Colo., and the radium will be extracted in Chicago. The company will mine ore from claims it has bought. The Standard Chemical Co. did no work on its claims except that required by law, but in this work produced and shipped a quantity of ore from its properties in Colorado and Utah, and purchased, it is stated, a considerable number of claims. It was reported in December that the company had produced a total of 14 grams of radium (elemental) and that its ore had averaged 1.7 per cent uranium oxide.

WANTED—I. C. S. graduate (young), with commercial experience, wants position as assistant chemist; reliable in inorganic analysis. Box 100, The Chemical Engineer.

The Chemical Engineer

PUBLISHED MONTHLY

at 608 S. Dearborn Street, Chicago, Illinois

Vol. XXIII.

CHICAGO, APRIL, 1916.

No. 4.

LABOR-**SAVING** PROBLEM OF CHILEAN NITRATE FIELD.*

By V. L. HAVENS.†

The nitrate fields of northern Chile lie, roughly, between 10° and 26° south latitude and have a width of 10 to 100 miles. It is not to be understood that all of the area embraced within these limits contains sodium nitrate in commercial quantities. On the contrary, there are vast areas where only the merest traces are occasionally found; but there are also many sections where the deposits are particularly rich, having depths of 3 to 5 ft. and a content of 50 per cent sodium nitrate. The nitrate is seldom found on the surface, generally being overlaid with 1 to 3 ft. of eolian soil; and although the ground is of a reasonably smooth character, there are many small hills and occasional stretches of hummocks, or rough ground.

The nitrate region is so arid that all fresh water must be brought from great distances in pipe lines. Salt water is occasionally found in wells. In 1912 there was a 20-minute shower—the first rainfall in many years.

From time to time the rights to the nitrate are sold at public auction. After one secures a tract sufficiently large to work on to advantage—of course, having prospected it thoroughly before buying—a reduction plant is erected at some convenient point. The cost of the reduction plant may vary from \$150,000 to twice that sum, depending on the number of boiling tanks required. Twelve tanks are considered to be a fairly large installation, although some "oficinas" have 24. In addition to this cost is that of laborers' quarters, office and residence buildings, carts, mules, and other equipment, track, engines, and many other things, depending on local conditions.

The first operation is that of extracting the "caliche," or nitrate-bearing mineral, rock, or soil, as one may care to name it. The extraction is done by individual contractors, who pile the rough blocks and pieces in regular piles for measurement. These piles are then loaded by contract laborers and hauled in carts or on decauville railways by day laborers to the crusher. After crushing to a size of about one-quarter inch the material is placed in elevated steel tanks, generally un-

der roof, and water and steam are admitted for boiling. Generally the boiling requires about four hours. The "caldo" (soup), as it is locally termed, is then drawn off and a small quantity of wheat flour is added, which causes the earth to settle, the caldo being carried to the open-air settling tanks. The nitrate is precipitated from this liquid, and the remainder is called "agua vieja," or old water.

The agua vieja is run into a tank, cut with acids, and iodine in the form of a red mud is precipitated. This mud is collected in burlap bags and pressed, the product being known as iodine cheese. The cheeses are removed from the bag, put in a porcelain-lined oven, and baked, and iodine crystals are taken out. Much of the agua vieja is returned to the boiling tanks and used several times, as losses are thus reduced, not only in unprecipitated content but also in water, which, being brought in pipe lines from 125 to 250 miles, is rather expensive.

Referring again to the settling tanks, after the agua vieja is drawn off, nitrate crystals, about 95 per cent NaNO_3 , 1 per cent NaCl , and 4 per cent hygroscopic water and lime or other extraneous sediment are left in the tank. This is shoveled onto small cars which run on a rail trestle and dump the product into the "cancha," or storage floor. Here sacks are filled by hand shovelers, each sack being supposed to contain 203 lbs.

The boiling tanks previously mentioned, where the raw material is treated with steam and water, have an enormous residue of worthless material remaining after each boiling. This is called "ripia," and consists principally of earth in various forms. It is dropped from the bottom of the tank into decauville cars and hauled out to the waste bank, which rapidly assumes gigantic proportions. The removal of the muck, or ripia, is a serious problem.

In addition to its nitrate-recovery installation each oficina has a powder mill, machine shop, power house, stables, general store, hospital, general offices, administration building, where the principal employes are housed, laborers' quarters, laundry, tailor shop, occasionally a hall for entertainment, possibly a band stand, and the various accessories required for a town of 500 to 1,000 laborers with their families.

The men who extract the caliche work under contract. Each is provided with all necessary tools and

*U. S. Commercial Attache, Santiago.
†From Daily Commerce Reports.

supplies, including dynamite, fuse, caps, black powder, 1/2-in. to 3/4-in. drill steel, drill-hole spoons, crowbars, 25-lb. square-faced sledge; a No. 2 Edwards (English) shovel, round pointed but rather flat and sometimes called "calichera" or "salitrera" shovel, and at times other small tools. Those named, however, form the standard set, but at times a laborer wants a smaller hammer in addition. All tools must be returned in reasonably good condition. The drill steel wears out and the company blacksmith sharpens it at no cost to the driller, but the driller must pay for the steel consumed. He must also pay for dynamite caps and fuse, but black powder is supplied to him free, it being very cheap and made by each oficina.

The drilling by hand is slow work in spite of the comparative softness of the ground, and within a reasonable length of time there should be a radical change in the system followed. The work is so scattered that air cannot be piped; the tank should be mounted on an auto truck and provided with several nozzles, so that the truck could stop at a given point, drill several holes, and get away without loss of time. There is no doubt that a very important economy can be introduced here. If the saving should be only a small one it would be important because the value of the finished product is low, seldom exceeding \$2 per 100 lbs. in normal times.

Any fuel which might be considered for use in developing power should be of low price, as gasoline, benzine, and fine grades of oil are very expensive in Chile. The writer has never seen such enormous numbers of men engaged in hand drilling even in countries of very low wage rates, and in the nitrate fields the most common Indian labor receives about \$1.50 United States gold per day. There are 170 oficinas in operation in Chile, and if they average only 100 men each in the pampa (which is a low estimate), and if these men drilled during only one-tenth of their time, it would mean 1,700 hand drillers working constantly. Experts who have devoted considerable time to a consideration of the problem state that if a satisfactory power drill were brought out its sales should aggregate over \$2,000,000.

No great economies appear possible in the selection of the caliche, as it involves judgment to a considerable extent and hand picking is necessary. However, if drilling is reduced considerably, an economy in the number of men employed would be felt, which would reduce the requirements for housing, medical attention, and superintendence.

The next step where labor wastage is noticeable is in getting the caliche to the crusher. Hand loading is practiced, and where decauville trains are used the haulage is comparatively a small item, but the first cost is great. Where mules and carts are used the first cost is reasonably large, and fodder is worth three times as much as in the United States. Mules 14 hands high cost \$160, three sets of single harness cost about \$100, and the cart perhaps \$120. The total first cost

is, therefore, approximately \$700, and the services of a driver cost \$1.50 per day. It is doubtful if the mules and equipment can be maintained, insured, and amortized under \$1.50 per day, or say the total cost of \$3 per day. The driver helps to load the caliche, and if he should drive a truck with trailers he could not help in the loading. However, his help might not be considered absolutely essential, since men are actually supplied to the individual contractor to load to decauville train and could load to trucks if trains and carts were dispensed with.

An auto truck would cost \$2,500 to \$3,000, but it is thought that the truck's ability to supplant both mules and locomotives is an important consideration, and there are already eight motor trucks on the way to the pampa from the United States. Any effort to increase the sale of motor trucks in this locality must be accompanied by a consideration of the use of low-grade oil, not gasoline. Also, it may be mentioned that the more progressive companies are getting rid of coal-burning apparatus in their power houses as rapidly as possible and are using crude oil, generally consisting of mixed residual oils from California and Peru.

After the caliche is delivered to the crushers (generally of the jaw type) and then elevated to the boilers there seems little chance for economy by alteration of equipment. It does appear that a longer boiling would extract more of the product sought, there being as high as 8 per cent of sodium nitrate left in many dumps, but the extraction of this would employ the tanks too long when they might be used to better advantage. The most easily obtained economy—which, after all, may not be worth while because of details not considered—would be in the conservation of heat from the tanks. Steam rises in the open air, the sides radiate heat continually, and at first glance one is apt to express surprise at the obvious waste of heat. However, the writer spent but a short time in the nitrate fields and does not by any means feel that he learned all the details of nitrate reduction.

In nitrate reduction, as in so many other industries, the disposal of the waste presents a crying need for greater economy. The introduction of belt carriage might not prove desirable because the delivery of the waste is not continuous and the product is wet; likewise the use of cableways or aerial trams might not be found satisfactory because of the cost of towers and the narrow bank that is usually built with them. The use of a donkey engine to draw the loaded cars to the top of the waste pile would seem to offer a convenient method of waste disposal, if not a complete solution of the difficulty. The problem is said to vary in each oficina, and may do so in the sense that the quantity of waste to be disposed of varies; but it is thought that a satisfactory solution at one plant would soon be adopted, or adapted, by others.

It is a matter of some surprise that North Americans secured no appreciable interests in the nitrate fields of Chile until very late. Since the United States

ranks third as a consumer of the product in normal times, it would seem highly desirable from an economic viewpoint that that country should be able to sell where purchases are made—and the nitrate oficinas constitute a valuable market for hardware, groceries, wearing apparel, industrial railways, harness, carts, steel and iron tanks, coal, oil, corrugated iron, and workmen's tools. Practically all the boilers are English; the oil-burning apparatus, most of the electrical apparatus, and many of the shop tools are German; but it is thought that American manufacturers should enjoy a reasonable share of the business if they are prepared to enter the market.

Although there is danger to the nitrate industry from the competition of nitrogen drawn from the air, this danger is directed principally against its use for explosives—which has in the past absorbed but 30 per cent of the output. Potash is said to have been found in reasonably large quantities in the nitrate fields; and if the deposits are as rich as reported, then the potash may be combined with the saltpeter to form potassium nitrate, the remaining sodium chloride may be abandoned, and enormous savings of transportation charges be introduced on the product destined for fertilizer. In addition to the nitrate of soda, the Chilean desert holds great deposits of sodium chloride, or table salt, borax, and numerous other substances. Along the foothills to the east are found enormous deposits of copper and sulphur, and water will be found because the snow-topped Andes always deliver water to the desert, but the lines of flow have not yet been determined.

As one travels along the West Coast of South America, he is apt to look with little favor on the desert or northern Chile. It is not appealing to the eye accustomed to green things, being naked and sun baked, but it holds the national wealth of Chile.

The mining of copper began in Alaska in 1901 and the total output of the metal to the close of 1915 is 219,913,375 pounds, valued at \$34,919,581. Of this amount, according to the statistics recently completed by Alfred H. Brooks of the United States Geological Survey, 86,500,312 pounds, valued at \$15,139,129, was produced in 1915. This is more than four times the output of 1914, and by far the greatest in the history of the Alaska industry. Thirteen Alaska copper mines were operated in 1915 compared with seven in 1913. A total of 300,600 tons of ore was mined in 1915 which, in addition to the copper, carried gold to the value of \$153,121 and \$455,204 worth of silver.

The twenty-first annual convention of the Fraternity of Operative Millers of America will be held in St. Louis, Mo., May 29 to June 3, 1916. An exhibition of flour and cereal-mill machinery and of allied lines will be held at the Coliseum in connection with the convention. It is estimated that 2,000 to 3,000 millers will attend the meeting.

ECONOMICAL METHOD OF PREPARING POTASSIUM-FERRI-CYANIDE SOLUTION DEVELOPED BY THE DEPARTMENT OF AGRICULTURE.

As a result of the great increase in the price of potassium-ferri-cyanide, or red prussiate of potash, which is extensively used as a coating material for blue-print paper, an economical method of preparing the substance has been devised by the Department of Agriculture. Before the beginning of the war, potassium-ferri-cyanide could be obtained for 55 cents a pound. It now sells for about \$6.00 a pound and, moreover, it is exceedingly difficult to obtain in this country even at that price. Since blue-print papers in this country are coated almost exclusively with potassium-ferri-cyanide and all coating, blue printing, and washing equipment is built for use with this as the coating material, the rise in price has worked quite a hardship upon both the producers and users of blue-print paper.

Potassium-ferri-cyanide is produced by oxidizing a solution of potassium-ferro-cyanide with chlorine gas. At the same time a small amount of potassium chloride is produced. Investigations by the Bureau of Chemistry show, however, that the presence of this amount of potassium chloride in the coating of the paper does not interfere with the color and durability of the print. It is unnecessary, therefore, to separate the potassium chloride by crystallizing the potassium-ferri-cyanide, provided that the latter is to be used on the spot and soon after it is prepared.

The apparatus devised by the Bureau of Chemistry for preparing in this way potassium-ferri-cyanide solution is simple. The chief precaution to be taken in its operation is to see that the finished solution does not contain an excess of chlorine. At the prevailing prices of the materials, potassium-ferri-cyanide solution can be made by this process at the cost of approximately \$2.80 per pound, calculated on the dry salt basis. At the prices which prevailed before the war and which may be regarded as normal, the cost would be approximately 35 cents per pound.

Allowing for possible loss, 100 lbs. of potassium-ferro-cyanide should yield about 75 lbs. of potassium-ferri-cyanide. Probably 10 lbs. of chlorine would be required also. That is, $1\frac{1}{3}$ lbs. of potassium-ferro-cyanide oxidized with approximately $\frac{1}{8}$ lb. of chloride, would yield 1 lb. of potassium-ferri-cyanide.

In February potassium-ferro-cyanide was quoted at \$2.00 per pound and liquid chlorine can be obtained in iron cylinders for 15 cents a pound. At these prices, as has already been said, a pound of potassium-ferri-cyanide in solution can be made for approximately \$2.80 per pound, whereas it is now quoted on the market at \$6.00 a pound.

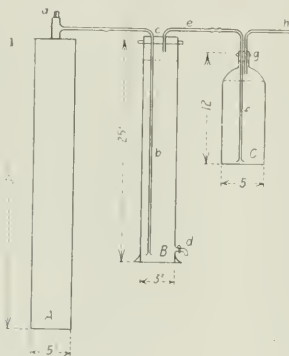
This saving is, of course, much greater than under normal conditions when technical potassium-ferro-cyanide can be obtained for 25 cents per pound and

technical potassium-ferri-cyanide for 55 cents per pound. The price of the potassium-ferri-cyanide, at all times will be greater than the price of potassium-ferro-cyanide, since the former is prepared by oxidizing the latter with chlorine followed by repeated crystallizations to separate the potassium chloride formed at the same time. It seems probable, therefore, that even under normal conditions the simple procedure devised by the Department of Agriculture for the preparation of potassium-ferri-cyanide solution will prove profitable for users of large quantities of blue-prints.

The necessary apparatus has been developed primarily for use in the government service, but it is equally available for other purposes. The method and apparatus for making potassium-ferri-cyanide are described as follows:

METHOD OF APPARATUS.

Apparatus.—This apparatus is designed to produce 1 lb. of potassium-ferri-cyanide from 1.33 lbs. of



Arrangement of Apparatus.

potassium-ferro-cyanide. *A* is a cylinder containing chlorine, *B* is a glass cylinder 3 ins. in diameter and 25 ins. in height, capacity approximately $\frac{3}{4}$ gal. (Eimer & Amend Catalog 2496), in which the solution of potassium-ferro-cyanide is placed. *C* is an ordinary acid bottle containing a solution of sodium hydroxid for absorbing any excess of chlorine which may be unabsorbed by the solution of potassium-ferro-cyanide. The glass cylinder *B* is fitted with a glass petcock (*d*) near the base for withdrawing a portion of the solution for testing completion of oxidation. At the top it is fitted with a 3-in. cork (*c*) sealed with paraffin having two holes to accommodate the glass tubes (*b* and *e*). One of these tubes (*b*) extends to the bottom of the cylinder and is blown at the end to well distribute the gas. It is connected by a short piece of rubber tubing to the pipe attached to the chlorine cylinder. The other tube (*e*) which does not touch the surface of the solution in cylinder (*B*) is connected by a rubber tube to a glass tube (*f*) running to the bottom of the acid bottle and blown to distribute any gas which may not be absorbed in *B*.

Bottle *C* is fitted at the top with a cork (*g*) sealed with paraffin and having two holes through which pass tubes. One of these tubes (*f*) runs to the bottom of the bottle, the other (*h*) starting from above the liquid is so connected as to carry unabsorbed chlorine out of doors. The chlorine gas is regulated by a valve (*a*) in the head of the chlorine cylinder. The glass tubing used should be $\frac{1}{8}$ in. inside diameter.

Operation.—Dissolve 1.33 lbs. of potassium-ferro-cyanide in about 2½ quarts of distilled water and pour into cylinder *B*. Nearly fill bottle *C* with a 10 per cent solution of caustic soda. Connect the chlorine cylinder with tube (*b*) by means of a short piece of rubber tubing and tube (*e*) with tube (*f*) and finally run a tube (*h*) from bottle *C* out of doors. Turn on the chlorine gas and allow it slowly to bubble through the solution of potassium-ferro-cyanide. Shut off the chlorine at intervals of a half hour or so and to aid the absorption of the gas shake or agitate the container. Do not allow the caustic soda solution to suck back when the gas is shut off. This can be prevented by breaking the connection between *B* and *C* immediately after shutting off the chlorine. Continue passing the chlorine into the potassium-ferro-cyanide solution for some time after the color has darkened considerably. After which frequent tests are necessary to determine when the oxidation has been completed. To test for complete conversion to the ferri-cyanide, draw off a little of the solution through the petcock (*d*), dilute with distilled water and test with a solution of ferric chloride. If a blue precipitate is formed potassium-ferro-cyanide is still present and the process must be continued. If a brownish or amber colored solution results, the oxidation is complete. After tests show the oxidation to be complete, turn off the chlorine gas, disconnect the chlorine cylinder and connect (*b*) with an air pressure line. Bubble air through the solution until no odor of chlorine is noticeable. In case air pressure is not available and suction can be obtained, break the rubber connection between tubes (*e* and *f*) and connect (*e*) with the suction and draw air through the solution until free of chlorine.

Great care must be exercised that no chlorine escapes into the room and comes in contact with the flesh as it is a powerful irritant and serious injury may result to the throat, nose, eyes and hands from exposure to the fumes or contact with the liquid.

A company has recently been organized in Lima, Peru, for the manufacture of cement, according to the Callao Revista Comercial of February, 1916. The price of cement in Peru has risen from \$3.40 to \$6.50 a barrel since the outbreak of the war on account of reduced shipping facilities and the closing of European markets from which Peru formerly took 50 per cent of its average annual cement imports of 94,380 barrels.

NITRATE OF SODA AND SULPHATE OF AMMONIA IN 1915.*

In introducing our review of the sulphate of ammonia and nitrate of soda markets for 1914, while apologizing for the incompleteness of the statistics we were then able to give, we expressed the hope that at the end of another year the international situation in Europe might be such as to permit of our writing our 1915 review more nearly on a level with those for other years. That hope has, unfortunately, been disappointed, and we are laboring under still greater disabilities in writing our present review.

The circumstances existing at the beginning of the year and the new factors which have come into play during the year have been so far abnormal that previous business experience has been practically useless for guidance. The year's experience, however, ought to make it possible to take more reliable views of the outlook than was the case twelve months ago, as there has been time for adjustment to the altered circumstances; but there will necessarily have to be a readjustment when the war comes to an end, and that time may conceivably occasion as many trying situations as the course of the war has disclosed.

We would again express the hope that before the time arrives for writing our next review peace may have been established on a solid and satisfactory basis.

NITRATE OF SODA.

The conditions which have prevailed during the past twelve months have been so far exceptional that they cannot be compared in any way with the conditions which have governed the market during any other period in the history of the trade. It would be useless therefore to attempt to establish any comparison between 1915 and the previous year, or any other year, or to reason on the lines we have hitherto followed. Moreover, inasmuch as complete figures representing deliveries, etc., in Europe are not obtainable, we think that it would serve no useful purpose to give the figures which are obtainable.

The outstanding facts in the situation at the end of 1914 were the stoppage of direct shipments to Germany and Belgium, unprecedentedly heavy stocks on the West Coast, and, on the other hand, a rapidly decreasing output. We may perhaps add the fact that in the United States there was a shortage of supplies, which was bound to be replenished early in 1915, though this fact was only of minor importance in relation to the other three. Demand for munition purposes had hardly made itself seriously felt. When we point out that the imports into Germany and Belgium in 1913 amounted to about 1,150,000 tons—or nearly twice as much as those into the rest of Europe, including Egypt, during the same period—it will be appreciated how serious a matter it was that such an outlet should be blocked. Of course, it was known that supplies would find their way indirectly into Germany and

Austria; but manifestly such supplies could not constitute a serious offset against the shrinkage in direct shipments to which we have referred. The West Coast stocks at the end of 1914 were estimated at about 1,120,000 tons—an increase of 625,000 tons during the year, and due largely, though not altogether, to the outbreak of war and consequent shrinkage in shipments. The increase in stocks up to the end of July had in fact been such that the curtailment of output was under consideration when the war broke out, and some thirty to forty oficinas had already been closed down. From that time up to the end of 1914 the process of closing down had been steadily proceeding.

The most prominent factors during the year have been the continued closing down of oficinas in the early months, and the reopening of them when the market improved, the phenomenal advance in freight rates, and the almost world-wide demand for nitrate of soda for munition purposes. By the end of March only about one-fifth of the total number of oficinas were still working, but these were the largest and strongest concerns, and, of course, they represented far more than the average oficina output capacity on the West Coast. Such drastic measures show the seriousness of the view which producers took of the situation brought about by the war. By the month of April, however, some impression had been made upon stocks on the West Coast, and the *free alongside* market, which for more than six months had been more dead than alive, had begun to revive, there being the large demand for the United States, which we anticipated, and demand for munition purposes everywhere. From April forward there was a well-sustained demand up to September, when the stoppage of the Panama Canal gave a further impetus to buying, and within a month a very large business resulted at up to 9s 7d per quintal. It was known that many cargoes were held up in the canal, and the buying was for the purpose of replacing the quantity so held up by shipments via the Cape. That the buying was hasty and ill-advised became clear when fresh chartering had to be done and it was found impossible to secure the necessary tonnage even at the further inflated freight rates which the fresh demand brought about. With advancing *free alongside* prices oficinas had re-opened, and at the close of the year the output is fully equal to the output before the war. Manifestly it has outstripped the world's requirements, including the very large requirements for munition purposes, with Germany out of the market, and we do not see that the inflated prices paid in October were justified even if freight room had been obtainable. Before October was out there was a relapse in prices, and at the close the value is not more than about 7s per quintal. Whether even 7s per quintal can be maintained is more than doubtful, unless producers very soon come to an agreement to curtail production all round. The matter has already been under considera-

*From Review of Bradbury & Hirsch, Liverpool, England.

tion by producers, and the market will await with keen interest the result of further negotiations.

Having regard to prices current in Europe and the United States, the year's working cannot be considered as very satisfactory from the point of view of producers. And although an advancing market must always be to the advantage of importers, it is doubtful whether their share in the present case has been as large as on the face of it would appear, though we think that they have good reason to be satisfied. Undoubtedly, the lion's share has gone into the pockets of shipowners, and this will be made abundantly clear if we sketch briefly the course of the three markets—the market in Europe (at Liverpool for the sake of convenience) the free alongside market, and the freight market.

From 10s per cwt. at Liverpool at the outset there was an advance to 10s 4½d per cwt. in January, to 11s per cwt. in February, to 11s 6d per cwt. in March, and to 12s 6d per cwt. in April. After advancing to 13s per cwt., there was a decline to 12s 6d per cwt. in May, and to 12s 1½d per cwt. in June. There was a recovery to 12s 3d per cwt. in July, and in August 13s 9d per cwt. became the price. There was a decline to 13s 4½d per cwt. in September, but in October there was an advance to 14s 4½d per cwt. All through November the price remained 14s 4½d per cwt., but in December it was put up to 15s 3d per cwt. The average price for the year works out to 12s 4½d per cwt.

When the year opened there was hardly a West Coast market at all, and the nominal value of *ordinary* quality was not more than about 5s 6d *per quintal, free alongside*. In February there was an improvement in tone and 6s per quintal became the quotation. There was a gradual improvement in March, and in April 6s 6d per quintal was paid. There was an advance to 6s 9d per quintal in May, to 7s in June, and to 7s 7d in July. In August 8s 3d per quintal was reached, and in September as much as 9s 3d per quintal was paid, the blocking of the Panama Canal and the necessity for replacing cargoes held up being the immediate cause. Up to 9s 7d per quintal was paid in October, but from that time there has been a steady decline and at the close the value is not over 7s per quintal. The average price for the twelve months is 7s 7d per quintal, but it is probable that actual results make a better show than that, as we think that less business would be done at the lower prices when the market was neglected than at the higher level when demand was good.

The nominal freight rates at the end of 1914 were about 30s and 60s per ton, for sail and steam respectively. By the end of February 51s had been paid for sail, while 65s to 70s per ton was being quoted for steam. The improved demand for nitrate of soda having, with the assistance of reduced output, begun to make an impression upon West Coast stocks, this was automatically reflected in the freight market, and

in April 60s per ton was paid for sail and 95s per ton for steam. In May there was a decline to 57s 6d per ton for sail, but through June, July and August the rate was fairly steady at about 65s per ton. The rate for steam had declined to 85s per ton in June and to 77s 6d per ton in July, but there was a recovery to 80s per ton in August and to 82s 6d per ton in September. The blocking of the Panama Canal led to extra demand for tonnage in October, especially for steam, which it was practically impossible to supply owing to the scarcity of available boats, and forthwith a big advance in rates was demanded. At the close there would probably be charterers at 85s per ton for sail and at 125s per ton for steam for early 1916 loading. It will thus be seen that the question of tonnage has been the governing factor in the nitrate of soda trade in 1915, and that if tonnage had been sufficiently plentiful there would have been an abundant supply of nitrate of soda for all purposes, to the great advantage of producers and consumers alike. But in this respect the nitrate of soda trade has not been singular, as in most other trades advanced prices have been due to scarcity of tonnage and consequent inflated freights more than to anything else.

When we leave retrospect to deal with prospects we find ourselves in a dilemma, and this will be appreciated when we say that it is impossible to describe even the present situation with any degree of exactness. It is, for example, impossible to ascertain what the stocks of nitrate of soda in European ports amount to. It is impossible to ascertain even approximately what the quantity used for munition purposes in 1915 has been, or what it is likely to be in 1916. Although it is anticipated that the Panama Canal will be re-opened at the end of January it is quite possible that that estimate may prove to be inaccurate when regard is had to the stupendous job the repair has proved to be and the chances of the unexpected happening. It is, however, quite obvious that it will make an important difference to the European market whether the canal is re-opened at the end of January or a month or two later, as the re-opening will not only liberate the cargoes of nitrate of soda which have been held up since September but also open this shorter route for further shipments.

Although we cannot attempt to prognosticate in the absence of sufficient data to work upon, there are several facts which seem to us to have a bearing upon the present situation, and may therefore be worth mentioning. We find, for example, that the exports from the West Coast to Europe (including Russia) in 1915 have been something over a million tons, against less than two million tons in 1913, when Germany and Belgium together took nearly two-thirds of the whole. The margin provided for munition purposes by the shipment of upwards of a million tons in 1915 would seem to be more than sufficient had the Panama Canal not been blocked, and but for that accident we hardly think that we should have seen such

an advance in prices as has occurred within the past three months. Then, shipments to the United States in 1915 have been about 800,000 tons—nearly 200,000 tons more than the shipments in 1913, and nearly 300,000 tons more than the shipments in 1914, when the United States ran rather under par in the matter of supplies. From this we would argue that at the present time the United States are probably well supplied, notwithstanding increased use for chemical purposes, and that they will be less keen to compete for available tonnage on the West Coast than will buyers for the European market.

If the Panama Canal is re-opened at the end of January, as anticipated, there may be a chance of easier prices as larger supplies become available, but, otherwise, we think that even a higher level of prices may be reached before the spring months are over, seeing that the Cape route takes about twice as long for a voyage as the route by the canal, and that, therefore, a boat cannot do anything like the same amount of work. The time taken in loading and discharging is of course the same in both cases. The stocks on the West Coast are estimated to be about 800,000 tons. They are still increasing, and there will be no indisposition on the part of producers to sell, but so far as the European market over the spring months is concerned nothing will depend upon that.

SULPHATE OF AMMONIA.

In our concluding remarks upon the situation at the end of 1914 we expressed the opinion that we might dismiss Continental production from our consideration, inasmuch as it could only find its way to the world market through Holland and Italy even if supplies were available, and that it was not likely that exports on any extensive scale could be sent through those countries under the conditions then existing. This view necessarily led us to the further conclusion that the prospects of the market must be considered from the point of view of output in the United Kingdom

and the United States, the output outside those two countries and available not being enough to have any appreciable effect upon the market. Seeing, too, that more than the whole output in the United States is always required for home consumption, we thought that the problem might be further narrowed, and considered solely from the point of view of the United Kingdom supply.

From the above starting point we had to consider the prospect of an adequate demand, and, in the first place, it seemed to us likely that the stoppage of shipments to Germany and Belgium might be balanced by larger demand from France, Italy, and Spain, since all of these countries had drawn some supplies from Germany in 1914. Then, the exports from Germany and Belgium to Holland and the Dutch East Indies, January-April, 1914, were nearly 30,000 tons, and if our opinion that Germany would not have any sulphate of ammonia to spare in 1915 was a correct opinion it followed that Holland and the Dutch East Indies would have to depend upon the United Kingdom for supplies. It was within our knowledge that buyers in the United States had had to cancel contracts for German output, but it had also transpired that they were cancelling contracts with the United Kingdom, so that it did not necessarily follow that British output would have to be substituted for the German shortage in the early months of 1915. The cotton-growing industry in America was in fact in such a demoralized condition that it was by no means clear what the upshot of the campaign in that country might be, but the prospects were by no means bright. There had been a heavy falling off in shipments to Japan during the preceding six months, and it was not possible for the market to count with confidence upon that country for support over the coming season. There was, however, in the price of sugar and in prices of all cereals every inducement to fertilize on the most liberal scale outside the war area, and inas-

TABLE I.—SHIPMENTS OF SULPHATE OF AMMONIA FROM UNITED KINGDOM, 1910 TO 1915.

January-December.	1915. Tons.	1914. Tons.	1913. Tons.	1912. Tons.	1911. Tons.	1910. Tons.
To France	11,430	2,486	8,964	7,665	7,239	8,437
To Germany		3,427	9,388	1,843	2,740	7,070
To Belgium		1,032	5,169	31	125	438
	11,430	6,945	23,521	9,539	10,104	15,945
To Spain and Portugal.....	65,057	59,863	55,920	61,460	56,501	50,241
To Italy	7,071	5,060	5,822	13,542	10,162	10,202
To Canaries	4,985	7,932	8,495	8,148	7,131	6,673
	77,113	72,855	70,237	83,150	73,794	67,116
To Holland	32,191	9,074	2,872	2,216	3,352	3,411
To Java	93,496	54,869	38,046	33,554	28,168	32,362
To British Guiana.....	8,262	8,578	7,371	6,493	7,808	7,532
To West Indies.....	20,230	7,299	6,810	4,039	5,820	5,271
To Mauritius	7,795	6,690	5,176	6,573	5,966	6,009
	161,974	86,510	60,275	52,875	51,114	54,589
To Japan	10,537	87,776	114,684	86,659	76,095	57,360
To United States.....	16,377	43,651	37,067	39,333	65,920	76,111
To Other Countries.....	16,877	16,140	18,920	15,308	14,856	12,651
Total Exports	294,308	313,877	324,704	286,864	291,883	283,772

much as nitrate of soda does not seriously compete with sulphate of ammonia outside the Continent, unless in the United States, we anticipated a still higher level of prices for sulphate of ammonia over the spring months of 1915, German output not being available.

In order that our friends may see how far our anticipations were justified, it will be convenient at this point to insert the tables of exports, which we have made up as heretofore. Of course, new factors came into play to disturb our calculations; but we will comment upon these at a later and more appropriate stage.

The exports of sulphate of ammonia from the United Kingdom for the years 1910 to 1915, inclusive, are given in Table I.

It is perfectly clear from the figures that had Japan been buying on anything like her previous scale there must have been a sulphate of ammonia famine and corresponding prices, whilst, with Japan almost out of the hunt, but for the intervention of Holland and Sweden there must have been a glut of supplies and a slump in prices. It has been attempted to show that the excess quantity taken by Holland and Sweden up to the end of March—25,039 tons—and which occasioned the action of the government, already referred to, was required to replace what had been taken from Germany in other years, but the figures are altogether against the contention, the Dutch import from Germany, January-April, 1914, having been only 11,946 tons, and in 1913 only 9,238 tons, whilst Sweden took none. Under the conditions prevailing, we do not think that a shrinkage of only 4,468 tons in the total shipments from the United Kingdom over the six months can be regarded as other than satisfactory.

The total shipments to Java from the United Kingdom in 1915 have been 93,496 tons—figures never even approached when that country was exclusively supplied by the United Kingdom. The shrinkage of a further 37,270 tons in the shipments to Japan was not unexpected, but the shrinkage of 19,659 tons in those to the United States is not so easily explained. There has, of course, been a very substantial increase in the home production, and this has all along been "up against" British production; but it seems likely that the smaller cotton crop aimed at, in view of Germany being substantially out of the market, has also been a factor in the case. Of course, the United States have within the year imported much larger supplies of nitrate of soda, and these may to some extent have ousted sulphate of ammonia, but we think that the increase has been very largely used for other than agricultural purposes.

If the exports for the whole year are compared with the exports in 1913 it will be seen that the entire trade has been turned upside down by the war, either directly or indirectly. The exports to the Continent have shrunk from 23,521 tons in 1913 to 11,430 tons in

1915, those of Japan from 114,684 tons in 1913 to 10,537 tons in 1915, and those to the United States from 37,607 tons in 1913 to 16,377 tons in 1915, whilst the shipments to Holland and the sugar-growing colonies have increased from 60,275 tons in 1913 to 161,974 tons in 1915, and home consumption (for all purposes) from 105,000 tons in 1913 to 128,000 tons in 1915. Exports to Spain have also increased substantially, and they would have made a still better show if permits to ship had been granted more freely.

No recent year has opened under more favorable conditions, from the British sulphate of ammonia manufacturers' point of view, than the year 1915. With Germany out of the competition, and with the prospect of exceptional demand for the sugar-growing colonies, the way to ample demand and to higher prices seemed to be quite clear from the outset. Probably the advance from £12 2s 6d to £13 13s 9d per ton in January was more than was expected, having regard to the mild fluctuations which the market had been accustomed to over so many years. The setback to £13 12s 6d per ton in February, to £13 10s per ton in March, and to £13 8s 9d per ton in April, was due in the first instance to the defection of Japan and the United States, but it was contributed to in April by government intervention in regard to shipments to Holland and by the inadequacy of railway and shipping facilities, the shrinkage in the total shipments up to the end of April, compared with the shipments January-April, 1914, being no less than 10,032 tons. Belated shipments, more particularly those to Spain, were, however, made good in May and June, and there was a recovery to £13 17s 6d per ton in May and to £14 8s 9d per ton in June, by which time government requirements for munitions had begun to make an impression.

By the end of the first week in July the upward movement had spent itself, belated shipments having been disposed of and there being no other special demand, and the market was quiet up to the close, when the price was £14 13s 9d per ton. Owing mainly to the difficulty in obtaining shipping permits from the War Trade Department and to the hesitancy of buyers abroad about placing further orders, the price gradually declined to £14 10s per ton in August. There was very little fluctuation during the month of September, and at the close £14 10s per ton was still the price. In October, however, there being a well-sustained demand, there was a steady and rapid advance from the outset up to the close, when £15 7s 6d per ton had been realized. By this time government requirements for munition purposes had become a real factor in the situation, and the reservation, at the instance of the Board of Agriculture, of a proportion of the output of sulphate of ammonia for home agricultural purposes had also to be taken account of by buyers. Moreover, the government strings controlling shipments to Holland had been slackened. The consequence was a strong demand from practically all

foreign markets, excepting the Japanese, and an advance in prices up to £16 7s 6d per ton—the highest point reached since 1883.

The average price for January-June was £13 10s 7d per ton, or £1 13s 3d per ton above the average price for January-June, 1914. The average price for July-December works out £15 4s 7d per ton, or £4 7s 9d per ton above the average price for July-December, 1914. The average price for the year is therefore £14 7s 7d per ton, or £3 0s 6d per ton above the average for 1914, and we have to go back as far as 1884 to find a higher average price in any year, viz.—£14 9s 3d per ton. Of course, such a result can only be attributed to the accident of war, whereby Germany, which country had become a very serious competitor with the United Kingdom in the world market, has been out of the running. The high average price has, moreover, to be very substantially discounted to cover the inflated cost of acid, coal, labor, etc., but, when full allowance is made to cover the increased cost of manufacturing, the net result must be considered to be highly satisfactory, though not as satisfactory as the result in 1912, when the cost of manufacturing was about normal, but the output largely affected by strikes.

The output in the United Kingdom in 1914 proved to be 426,000 tons—a decrease of 6,000 tons upon the output in 1913, there having been a decrease of 6,000 tons from gas works and of 4,000 tons from iron, against an increase of 4,000 tons from carbonizing, etc.

We find it impossible to estimate with much confidence the output during the past year, there being scarcely a single industrial concern or a gas works which has not been affected for better or worse by the war conditions which have existed. Our friends engaged in production from the different sources have, however, been extremely kind, as usual, in furnishing us with figures and opinions, and we think it well to give the conclusions at which we have arrived.

Sulphate of Ammonia Production in Great Britain
—Production of ammonia, calculated into sulphate of ammonia (including that used in the manufacture of ammonia soda, munitions and for other chemical purposes), from all sources in the United Kingdom during 1915, we estimate, with all reserve, at 423,000 tons, viz.:

	Tons.
Gas works	173,000
Iron	16,000
Shale	58,000
Coke and carbonizing works and producer gas.....	176,000
	423,000

Of this quantity we estimate that—

	Tons.
England contributed.....	302,000
Scotland	118,000
Ireland	3,000

The production during the previous five years is given in Table II:

	TABLE II.				
	1914.	1913.	1912.	1911.	1910.
Gas works.....	176,000	182,000	172,000	169,000	168,000
Iron	16,000	20,000	17,000	20,000	20,000
Shale	63,000	63,000	62,000	61,000	59,000
Coke and carbonizing and producer gas	171,000	167,000	137,000	135,000	120,500
	426,000	432,000	388,000	385,000	367,500

Our estimate of production in the United Kingdom in 1914 was 5,000 tons under the mark, the shrinkage in the output from carbonizing, etc., during the first half of the year having been more than balanced by the larger output in the second half. We are satisfied that our estimate of stocks at the end of the year was substantially correct and that the increased output disappeared in home consumption of munitions. On that assumption the account for 1915 will stand as follows:

	Tons.
Stocks brought forward from 1914.....	25,000
Production in 1915.....	423,000
	448,000
Exports during 1915.....	294,000
Home consumption (for all purposes) 1915.....	138,000
Stocks to carry forward into 1916.....	26,000
	448,000

SULPHATE OF AMMONIA PRODUCTION IN UNITED STATES.

Production of ammonia calculated into sulphate of ammonia in the United States during 1915 is estimated by The American Coal Products Company to have been 212,000 tons—an increase of 17,000 tons upon the actual output in 1914. It is, further, estimated that something like 79 per cent of the 1915 output has been from by-product coke ovens, and in view of the keen demand for coke and for the by-products it seems certain that a further substantial increase in the output of sulphate of ammonia in the United States must be counted upon in 1916. For the same reason and for other reasons we think that there will be an increased output in the United Kingdom in 1916, but it is quite impossible to estimate what it may amount to. There will no doubt be some increase in production in Japan and other countries, but as this will not come on to the world market excepting to slightly limit demand upon the United Kingdom supply we may proceed to the consideration of the outlook from the point of view of the United Kingdom supply alone as we did at the end of 1914, more than the entire output in the United States being required for home consumption.

What, then, are the chances of the market over the coming season? It may help to clearness of vision if it is remembered that the shrinkage in shipments was about 36,000 tons to Japan and the United States, January-April last, compared with January-April, 1914, and that this shrinkage was practically balanced by the increase in shipments to Holland, Java, and Sweden over the same period. And, seeing that we are of opinion that the course of the market may eventually depend upon shipments to the above-named countries over the next four months more than upon anything else—excepting perhaps home demand for

munitions—we think it well to discuss the chances of larger or smaller shipments in some detail.

Although there was a shrinkage of about 30,000 tons in the shipments to Japan and the United States, January-April last, these two countries took between them nearly 16,000 tons during that period. So far as we can judge they are not likely to take more than half as much over the next four months. Against the increase of 30,000 tons in the shipments to Holland, Java, and Sweden, January-April last, it may safely be assumed that Sweden will get none—against rather less than 5,000 tons last season.

The quantity permitted to be supplied to Holland will be determined by the War Trade Department, and, inasmuch as the brake was applied rather sharply when 21,155 tons had been reached at the end of March last, we think that we may also assume that the intention is to reduce the limit for the next three or four months.

In dealing with the case of Java we think that we should take a longer period than the four months, January-April, for comparison, because she is further away from the market and has quite obviously been anticipating her requirements. We find that shipments, July, 1914-April, 1915, when Germany was not in competition, amounted to 48,035 tons against 23,799 tons for July, 1913-April, 1914, when Germany was competing—an increase of 24,236 tons. We further find that against 48,035 tons which Java took, July, 1914-April, 1915, she has from July up to the end of December taken no less than 58,814 tons—that is to say, 10,779 tons more than she took altogether July, 1914-April, 1915. In view of this, is Java over January-April, 1916, likely to require very much of the 20,491 tons which she took January-April, 1915? We think not, after making every allowance for the stimulant of the famine price of sugar.

Spain will take larger quantities no doubt, as will also the West Indies and other sugar-growing countries, but not more than enough to compensate for the shrinkage in Japanese and United States demand which we anticipate.

From the point of view, therefore, of probable external demand over the coming season we do not see that any higher level of prices is justified. We must cast our eyes upon the home situation if we are to understand the rapid upward movement in prices which has been going on since the beginning of October. The demand for ammonia for munition purposes which has been steadily increasing during the past nine months is a new factor in the case. It is, of course, impossible to get any exact estimate of what this demand now amounts to per month, but in coming months it is certain that it will be out of all proportion to any increased output there may be. Then, as we have already pointed out, pressure has been brought to bear upon producers to reserve a proportion of their output for direct sale to farmers, at preferential prices, in order to induce a larger home

consumption. Whether the scheme will achieve the object intended we are inclined to doubt, because, as hitherto, this same trade has been provided for by manure manufacturers and local distributors by purchases and preparation made in advance.

The farmers are therefore being catered for from two sides which are bound to come into conflict, and it does not seem likely that manure manufacturers and local distributors will let the business slip through their fingers—especially if that evolves the carrying of their stocks forward to another season. However that may be, there can be no question that the reservation itself on top of actual requirements for munition purposes made a decided impression upon the minds of buyers both at home and abroad, the effect of which has been seen in the shape of exceptionally heavy purchases within the past three months for delivery ahead, it being realized that requirements for both purposes would be a first call upon the supply. There has been another reason for this heavy purchasing. Last season's experience has not been lost upon buyers abroad. If freight room was insufficient over the vital months last spring it is likely to be still more limited in 1916. If freight rates had advanced last spring they are on a still higher level now, and they have probably not yet reached the ultimate. It is not surprising, therefore, that buyers abroad should wish to avoid the losses and the inconveniences to which they were subjected last season, and be anxious to anticipate their prospective requirements by a month or more. That is exactly what they have been doing, and this action has no doubt contributed materially to the recent advance in prices. So far as this policy has succeeded it will follow that requirements will be smaller later on, but that cannot affect in the meantime the situation which has been created.

The question of the supply of sulphuric acid will become more acute as demand for ammonia for munition purposes increases, and there must be some shrinkage in the output of sulphate of ammonia, but, inasmuch as the munitions department can make use of concentrated liquor in place of sulphate of ammonia, the shrinkage in the actual output of sulphate of ammonia does not require to be allowed for in this calculation. It has been taken account of in requirements of ammonia for munition purposes. We do not see in the actual circumstances reason to doubt the stability of the market for some way ahead at least, but if, as we suggest, buyers have, on the advancing market, bought more heavily and for earlier delivery than usual, there may possibly be a set-back in prices when the summer months are reached. The extent of demand for munition purposes will probably settle the latter point.

SULPHATE OF AMMONIA PRICES.

Following are the average yearly prices of sulphate of ammonia from 1906 to 1915, inclusive, graded as good grey, 24 per cent, f. o. b. Hull, per ton:

Year.	£.	s.	d.	Year.	£.	s.	d.
1906.....	12	0	9	1911.....	13	15	3
1907.....	11	15	8	1912.....	14	7	9
1908.....	11	12	0	1913.....	13	7	8
1909.....	11	5	0	1914.....	11	7	1
1910.....	12	3	2	1915.....	14	8	1

Following are the average prices of sulphate of ammonia by months for the year 1914, good grey, 24 per cent, f. o. b. Hull, per ton:

Year.	£.	s.	d.	Year.	£.	s.	d.
1915.....	12	19	3	July.....	14	13	3
January.....	13	13	5	August.....	14	10	11
February.....	13	10	8	September.....	14	10	0
March.....	13	7	6	October.....	14	19	3
April.....	13	14	3	November.....	15	18	1
May.....	14	0	7	December.....	17	0	0

Following are the average prices of sulphate of ammonia from 1867 to 1905, inclusive:

Year.	£.	s.	d.	Year.	£.	s.	d.
1867.....	11	10	0	1887.....	11	17	8
1868.....	14	10	0	1888.....	11	18	0
1869.....	15	15	0	1889.....	12	1	4
1870.....	16	0	0	1890.....	11	9	0
1871.....	19	0	0	1891.....	10	15	5
1872.....	21	0	0	1892.....	10	1	10
1873.....	18	3	9	1893.....	12	11	4
1874.....	17	2	6	1894.....	13	3	8
1875.....	18	10	0	1895.....	9	15	4
1876.....	18	12	6	1896.....	7	18	0½
1877.....	19	16	3	1897.....	7	18	5
1878.....	20	5	0	1898.....	9	9	7
1879.....	18	8	9	1899.....	11	5	10
1880.....	19	0	0	1900.....	11	2	0
1881.....	20	4	6	1901.....	10	11	4
1882.....	20	8	6	1902.....	11	16	3
1883.....	16	11	0	1903.....	12	9	2
1884.....	14	9	3	1904.....	12	3	8
1885.....	11	9	1	1905.....	12	10	9
1886.....	11	3	7				

NITRATE OF SODA PRICES.

Following are the average yearly prices of nitrate of soda from 1906 to 1915, inclusive, in Liverpool (95 per cent) per cwt.:

Year.	s.	d.	Year.	s.	d.
1906.....	11	4	1911.....	9	10¾
1907.....	11	2	1912.....	11	1
1908.....	10	2½	1913.....	11	1
1909.....	9	9	1914.....	10	2½
1910.....	9	4½	1915.....	12	7½

Following are the average prices of nitrate of soda by months for the year 1915, in Liverpool (95 per cent) per cwt.:

Year.	s.	d.	Year.	s.	d.
1915.....	10	2½	July.....	12	2
January.....	10	10½	August.....	13	0
February.....	11	3¾	September.....	13	6¾
March.....	12	2	October.....	14	0
April.....	12	10	November.....	14	14½
May.....	12	2	December.....	15	0

COMPARATIVE PRICES.

Following are the comparative weekly prices of nitrate of soda and sulphate of ammonia, during 1915:

		Sulphate ammonia		Nitrate of soda	
		per ton.		per ton.	
Week ending.		£.	s. d.	£.	s. d.
Jan.	2.....	12	2	10	0
"	9.....	12	10	10	2
"	16.....	13	0	10	5
"	23.....	13	10	10	5
"	30.....	13	13	9	7
Feb.	6.....	13	15	0	10
"	13.....	13	13	9	11
"	20.....	13	12	6	11
"	27.....	13	12	6	11
Mar.	6.....	13	11	3	11
"	13.....	13	11	3	11
"	20.....	13	10	0	11
"	27.....	13	10	0	11

April 3.....	13	7	6	11	15	0
" 10.....	13	7	6	12	0	0
" 17.....	13	6	3	12	7	6
" 24.....	13	8	9	12	10	0
May 1.....	13	10	0	13	0	0
" 8.....	13	12	6	13	0	0
" 15.....	13	15	0	12	17	6
" 22.....	13	16	3	12	17	6
" 29.....	13	17	6	12	10	0
June 5.....	13	17	6	12	5	0
" 12.....	13	18	9	12	5	0
" 19.....	14	0	0	12	2	6
" 26.....	14	6	3	12	0	0
July 3.....	14	12	6	12	0	0
" 10.....	14	12	6	12	2	6
" 17.....	14	13	9	12	5	0
" 24.....	14	13	9	12	5	0
" 31.....	14	13	9	12	5	0
Aug. 7.....	14	12	6	12	10	0
" 14.....	14	11	3	12	15	0
" 21.....	14	10	0	13	0	0
" 28.....	14	10	0	13	15	0
Sept. 4.....	14	11	3	13	15	0
" 11.....	14	10	0	13	15	0
" 18.....	14	10	0	13	7	6
" 25.....	14	8	9	13	7	6
Oct. 2.....	14	11	3	13	10	0
" 9.....	14	15	0	13	10	0
" 16.....	15	0	0	14	5	0
" 23.....	15	2	6	14	7	6
" 30.....	15	7	6	14	7	6
Nov. 6.....	15	12	6	14	7	6
" 13.....	15	15	0	14	7	6
" 20.....	16	0	0	14	7	6
" 27.....	16	5	0	14	7	6
Dec. 4.....	16	12	6	14	12	6
" 11.....	17	0	0	14	17	6
" 18.....	17	2	6	15	5	0
" 25.....	17	5	0	15	5	0

ADVANCE IN ENGLISH DYEING PRICES.

The U. S. Consul at Bradford, England, in a report under date of Oct. 8 states that the Bradford Dyers' Association (Ltd.) has issued to its customers a circular stating that, in consequence of the serious position of the supply of dye wares and chemicals, it becomes necessary to make certain alterations in terms, conditions, and prices. For all goods and orders received on and after Oct. 12 to Nov. 30, 1914, inclusive, the association's prices for dyeing cottons—all prices existing on Sept. 30. For all goods and orders received after December 1, 1914, and until further notice, the prices of blacks will be increased by 10 per cent and colors 20 per cent on prices existing on blacks and colors—will be advanced by 5 per cent on September 30. The association also asks for indulgence in delivery, owing to the difficulty of maintaining regular employment at its works. Customers are assured that this advance of prices has been rendered necessary by the enormous increase in prices of supplies.

Standard Density and Volumetric Tables.

A revised edition of its Circular No. 19 on "Standard Density and Volumetric Tables" has just been issued by the United States Bureau of Standards. It contains tables for use in measurements of density and volume of such liquids as water, alcohol, sugar solutions, petroleum oils, etc., and special tables for use in the calibration of glass volumetric apparatus and hydrometers. In the new edition the tables have been rearranged and several new ones added.

DISPOSAL OF GAS HOUSE WASTES.*

By PAUL HANSEN.

Persons engaged in the manufacture of illuminating gas, as a rule, do not appreciate fully the objectionable results of discharging unpurified liquid gas wastes into sewers and water courses; partly because they have become accustomed to gas odors, and partly because the wastes give rise to conditions in sewers and waterways that would not be readily anticipated from their appearance. It will be the object of this paper to state briefly the objectionable effects produced by gas house wastes, and to describe methods for preventing these effects.

Wastes vary greatly in quantity and character, due to variable recovery of useful constituents and to the use of variable quantities of water. Generally speaking, the quantity of wastes per 1,000,000 cu. ft. of gas manufactured is greater and more offensive in the smaller plants than in the larger ones because of the smaller recovery of marketable products and greater waste due to leaky tanks and defective apparatus.

There is very little reliable information on the quantity of waste liquors from gas plants. From the fragmentary data available it would appear that the volume of wastes from a water gas plant may vary anywhere from 5,000 gals. to 25,000 gals. per 1,000,000 cu. ft. of gas produced. Coal gas plants generally produce smaller volumes of liquid wastes than do water gas plants. In most instances the volume of wastes can be greatly reduced by re-using the watery liquids after tar and oil has been partially separated in suitable reservoirs.

Wastes from gas plants are of a brownish yellow color somewhat turbid with more or less tarry sediment and floating oils. The waste liquids from water gas plants are generally clearer than those from coal gas plants, but they carry more light oil and have a more penetrating odor. Odor of gas wastes may always be detected in dilutions up to one in 5,000, and very often in much greater dilution than this, which accounts for the objectionable pollution of comparatively large streams.

The total solids as represented by residue on evaporation vary, according to examinations made by the Massachusetts State Board of Health, the New Jersey State Board of Health and the Illinois state Water Survey, from 1,000 to 52,000 parts per million. For the larger plants where efficient sedimentation tanks are used, the total solids should not exceed 6,000 parts. While this figure represents only six-tenths of 1 per cent of the volume of the liquid, a seemingly very small figure, nevertheless these matters are capable of many ill effects.

One of the most frequent complaints is that of tarry deposits on stream beds, wharves, retaining walls and the bottoms and sides of water craft. The deposits are unsightly, give off odors, especially when the water

is disturbed, and render waterways unfit for bathing purposes. When a waterway is also polluted with sewage, the tarry deposits entrain and hold sewage matter, which putrify and add greatly to the nuisance.

When gas wastes are discharged into city sewers the tarry matters adhere to the sides and bottom, sometimes resulting in complete clogging, or in any event seriously interfering with the flow of the sewage, and hence decreasing the capacity of the sewers. This difficulty is so great that sanitary engineers are generally agreed that crude gas wastes should not be permitted in public sewage. The same tarry wastes interfere very seriously with sewage treatment works by adhering to filtering materials and operating devices.

The floating oils in gas liquors spread out on the surface of water causing unsightly appearances and pronounced odors. Oils, especially in wastes from water gas plants, are very penetrating. In this connection it should be remembered that very little oil is required to cover a large surface of water. A drop of oil such as that used in gas plants is sufficient to cover the surface of the water in a full wash basin.

Gas liquors, especially the oils from water gas plants, have a highly toxic effect on fish. Experiments conducted by M. C. Marsh of the United States Bureau of Fisheries, indicated that dilutions of oil from water gas waste as great as one part oil to 400,000 parts of water, proved fatal to perch. The watery wastes and wastes in general from coal gas plants were less toxic, but dilutions as high as one to 100,000 are distinctly dangerous.

Even much greater dilutions than the above are decidedly objectionable where fish is concerned, in that they impart a disagreeable taste to the flesh. This difficulty reaches very serious proportions at Beardstown, Ill., where fishing is an important industry. It is customary at this point to keep the fish in "live boxes" along the water front of the city until shipment can be made. Although the gas wastes escaping into the river amount to but a few gallons per day, and although the river is large, entire catches are rendered offensive as food, even after cooking, by a "gassy" taste.

A similar effect on fish has been complained of at Rock Island, where fishermen claim that fish caught as much as 12 miles below the outlet of the gas house drain are at times affected with a "gassy" taste.

Oily films may also act to deprive fish of a proper supply of oxygen, but when oily films are so extensive the concentration is so great that fish are more likely to be killed by direct poisoning. In streams otherwise polluted, as with sewage, the principal effect of oily films, aside from their own direct offensiveness, is to prevent oxygenation of the underlying water, thereby promoting putrefactive decomposition, and thus intensifying nuisances from other causes.

The only extenuation in favor of oily films that can be offered is that when present in sufficient quantity

*Paper presented before Illinois Gas Association.

to cover quiescent water, they prevent the breeding of mosquitoes. This circumstance, however, happens too infrequently to be of any great moment.

Much has been said about the germicidal action of gas wastes, but their value in this connection has been greatly overestimated. While some germicidal effect may exist in the wastes from coal gas plants, it is very slight, and in wastes from water gas plants it is non-existent—in fact these liquids constitute a good culture medium, as evidenced by experiments by Whipple, for the New Jersey State Board of Health, in 1907.

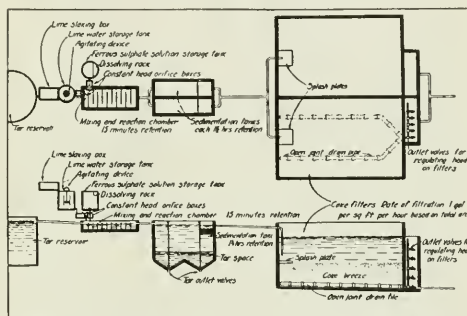
In all cases of pronounced stream pollution that have come to the attention of the state authorities of Illinois, gas wastes have been the basis of one of the principal elements of complaint. Along the Sangamon, below Decatur, for example, though the stream is grossly polluted with sewage and wastes from a starch factory, the odor and appearance of gas house wastes some times predominate for miles in a down-stream direction. At Galesburg, the gas house wastes add very materially to the gross pollution of Cedar Fork. In the Cuyahoga River, at Cleveland, and in the Chicago Drainage Canal, below Chicago, the self-purification of the stream has, at times, been more or less checked by oily films, which prevent access of atmospheric oxygen to the water below. The Passaic River, below Paterson, N. J., is one of the most notable examples of stream pollution by gas house wastes in this country. At Centralia, Ill., much complaint was made of tarry wastes adhering to the legs of cattle, and of the injury to soil and crops by tarry deposits.

Another bad effect of gas house wastes, which has here and there given rise to more or less serious trouble, is the pollution of the soil, which in turn gives rise to gassy tastes in well waters and to gassy odors in cellars. A striking instance of this occurred at Joliet, where one of the public water supply wells was affected with a gassy taste, which could be explained on no other basis than contamination from a gas plant near by. The writer had occasion some years ago to observe a similar instance of the long travel of gassy wastes at the town of Carthage, in Southern Ohio. Here the pollution was occasioned by coal tar wastes used at a tar paper factory. These wastes were permitted to flow into a pit at least 2,000 ft. from the affected wells. That large quantities of gas house wastes can enter the ground is strikingly shown by investigations made at the Lowell, Mass., gas works in 1905 and 1906, by A. T. Stafford and H. W. Clark, who estimated that there existed within the ground and within an area of a few acres, 1,600,000 gals. of tarry and oily wastes. Some of these consisted of accumulation in old drains and porous gravel, which, when tapped by excavations, flowed out in springs. Much waste was regularly finding its way into sewers, and from the sewers it entered cellars along the lines of the sewers at even remote distances from the works.

The first step in eliminating nuisance due to gas wastes is to reduce the volume of the wastes to a min-

imum and keep them well confined in channels and tanks. The volume of wastes should be kept down by re-using water after sedimentation for seal pots, and wherever else permissible; and by a strict separation of rain water drainage and wastes. This is particularly necessary in connection with gas holders. The overflow from gas holder seals is responsible for many cases of stream pollution. An instance of this is a small stream which flows through the campus of the University of Illinois.

After the volume of the wastes has been reduced to a minimum, which may be taken as 10,000 gals. per 1,000,000 cu. ft. of water gas, and about 6,000 gals. per 1,000,000 ft. of coal gas, then the wastes should be treated for the recovery of tar. This is usually accomplished by the use of tar reservoirs. These reservoirs should be of liberal size, not only to promote a



General Arrangement of Gas Wastes Treatment Plant.

good separation of tar and oil from the liquid, but also to equalize sudden discharges. A tank capable of holding several days' supply is desirable. The effectiveness of the tank may be increased by suitable placing of baffles, to secure complete displacement by the liquid passing from inlet to outlet, and also by heating the tank with steam coils. Very substantial concrete construction is desirable to prevent passage of liquids and tarry matter into the soil.

The effluent from the tar tank should next be treated with a coagulant. Ninety per cent lime in proportion of 3 to 4 lbs. per 1,000 gals. of waste treated is adequate for wastes from coal gas plants, but water gas wastes require coagulation with both copperas and lime to prove effective. Generally 2 lbs. of copperas per 1,000 gals. of waste are sufficient.

Correct preparation, storage and application of chemicals are very important items. The lime must be slaked in a suitable slaking box, and the hydrated lime thus obtained must be diluted to form a thin milk of lime (not over 5 per cent in strength) in order to prevent, as far as possible, clogging of pipes, valves and orifices. The milk of lime should be kept in a storage tank of suitable capacity, provided with a stirring device kept constantly in operation to secure a uniform suspension of lime particles. Uniform appli-

cation is secured by means of a small feed tank in which a constant level of water is maintained by a float operated inlet valve, and from which the chemical flows through a sharp edged orifice that should be made adjustable in size. Suitable feed boxes may be obtained from filter companies or they may, with comparative ease, be specially designed and built. Copperas is stored and fed in the same manner as the milk of lime, but being readily soluble, no stirring device is necessary. A convenient way of preparing a copperas solution is to place the crystals in a shallow box with perforated bottom, built in the side of the storage tank near the top, and spray water over the crystals until they are dissolved. A 5 per cent solution is of convenient strength.

To insure an intimate mixture and complete reaction of the chemicals with the wastes being treated, a highly baffled reaction chamber with a retention period of about 15 minutes is desirable.

Following coagulation, the wastes should be permitted to settle for a period of at least 1 hour. Rectangular tanks, with length about three times the width and depth of 5 or 6 feet, are best adapted to this purpose. It is always well to have the sedimentation tanks in duplicate so that one may be taken out of service when cleaning without disturbing regular operation. The tanks must, of course, be provided with suitable means for tar removal.

As a means for intercepting oil, a coarse coke strainer should be placed at the outlet of the sedimentation tanks. This can most readily be accomplished by building a shallow box with perforated bottom across the end of the tank about 9 ins. below the invert of the overflow channel and 2 or 3 ft. in width. The inner edge of the box should project above the level of the liquid in the tank. This box should be filled with nut size coke through which the wastes may pass in an upward direction. When the coke becomes clogged or saturated with oil, it may readily be shoveled out and replaced with fresh coke. The used coke can, of course, be burned under the boilers.

Very often the treatment above outlined will prove all that is necessary, but the effluent will still have some odor, color and turbidity, and perhaps there may be traces of oil. Nevertheless, it should not prove seriously objectionable if discharged into city sewers or into a stream of considerable size.

There are many cases, however, where a higher purification is necessary, and this is very apt to be true in the smaller plants where little or no attempt is made to recover valuable by-products such as tar and ammonia. Under such circumstances, final downward filtration through a bed of fine coke will produce an effluent so free from objectionable matters that it may be discharged into even the smallest water courses without giving rise to offensive conditions. Sand can be used quite as effectively as coke, but the coke has

the advantage about gas plants of availability and of being usable under the boilers after it becomes clogged. Suitable sand is not always available, and after removal from the filters it must be permitted to accumulate in unsightly heaps or disposed of at considerable expense.

The filter beds should be made 3 ft. or more in depth, of material not coarser than $\frac{1}{4}$ in. in diameter and free from fine dust. The area of the surface of the filter should be such that the rate of filtration will be about 1,000,000 gals. per acre per day, or roughly 1 gal. per square foot per hour. Under-drains of vitrified-tile laid with open joints should be placed across the bottom of the filters at intervals not greater than 10 ft. To prevent clogging of the drains, the joints should be covered with cheese cloth and the tile surrounded with gravel.

The surface of the filter must be kept level, and it should be, if possible, 4 or 5 ft. below the level of the outlet of the sedimentation basin, so as to permit this head of water on the filters before cleaning becomes necessary. When the filters become so clogged that water will not pass through them under the head available, the surface of the filter must be removed. Generally the removal of only a few inches of material will be necessary, as the clogging will take place principally at the surface. After successive scrapings have reduced the thickness of the filters to about 18 ins., there should be a deep scraping of at least 6 ins., and then new material should be placed to the original depth. Occasionally, it may be necessary to remove all the filtering material.

Times and means have not permitted the writer to canvass the country, or even the state, to learn what methods of purification are in use and how they are operating. At Lowell, Mass., there is a plant built along the lines indicated above and treating the combined wastes from the coal gas and the water gas processes, which is giving very good satisfaction, and has quite completely eliminated difficulties due to bad odors from sewers entering streets and houses. At Mendota, Ill., is a plant installed under the recommendation of the State Water Survey, but the construction in detail was not carried out as recommended, especially in the manner of applying the chemicals and use of the filter. Nevertheless, the treatment afforded has effected a very material improvement in the condition of Mendota Creek, into which the wastes are discharged.

In conclusion, it may be said that gas house wastes can generally be treated so as to overcome their offensiveness in a simple manner and at moderate cost. The problem at different gas plants unavoidably varies according to local practice, and in important cases it would be desirable, before expending any considerable sum on treatment works, to secure the advice of one who has given special study to purification of sewage and industrial wastes.



CHEMICAL TESTING IN SULPHITE PULP WORK.*

Your committee herewith respectfully submits certain proposed methods for testing raw materials used in the manufacture of sulphite fiber; also certain tests which have to do with the process itself.

It is our opinion that the standardization should be confined principally to the testing of raw materials, for the main purpose of supplying the purchasing department with information calculated to make for economy in buying; certain other methods of procedure can be included that are of such a general nature as to be used in all mills alike. It is in our opinion unwise to try to force all into the same mould. Each mill is individual and has particular problems of its own, a factor which should be fully taken into account in any consideration of the subject.

In our opinion the Technical Association of the Pulp and Paper Industry, through its various committees, should encourage mills to keep a systematic record of all of their operations; for it is by this method alone that true progress can be made in the art of manufacturing.

Technical knowledge is necessary, and every pulp and paper mill, regardless of its size, should have associated with it, in a responsible position, a man who is capable of understanding the nature of the scientific problems involved.

Careful records of the entire process, particularly with respect to the yields obtained under the different conditions of manufacturing, practically make of a mill one vast laboratory in which qualitative and quantitative work is going on continuously. Under the direction of a scientifically trained man the work would be co-ordinated, and in this way a certain element of mystery would be removed, and the organization protected from the disorganizing tendencies of the self-styled expert, who offers—usually for a consideration—to produce certain desired results, based upon what he claims to have done elsewhere. Expert advice can undoubtedly often be used to advantage, providing the mill organization is such that it is constantly recording its progress, through the careful keeping of records, as already suggested.

The problem of manufacturing is purely a matter of organization and this means detailed control of every part of the process, as well as a detailed record of each operation.

A freer exchange of ideas between the manufacturers themselves is much to be desired.

In conclusion, our committee recommends that standard methods for determining the quality of fiber be adopted, particularly with reference to color, strength and cleanliness, and it will gladly undertake to work out methods which can be universally adopted, with reference to the foregoing, as well as any other work which is placed under its jurisdiction.

ANALYTICAL METHOD FOR BLEACHING POWDER.

Sampling.—Upon notification of the arrival of a car, samples should be taken immediately from 5 to 10 per cent of the casks. The sampling is most easily carried out by driving a three-quarter inch brass tube through the cask, from end to end, and removing the powder held inside the tube. In this way a 1-quart mason jar will just be filled. This is then sealed and delivered to the laboratory, where the sample is immediately and rapidly quartered down to several ounces and all lumps smashed up fine.

Analysis for Available Chlorine.—A sample of from 3 to 5 grammes is weighed, using a weighing bottle, triturated with several portions of water, each portion being washed into 1,000 cc. volumetric flask and finally the mortar and pestle are washed clean into the flask and the volume made up to the mark.

Fifty to 100 cc. are then pipetted into 200 to 300 cc. of water in an Erlenmeyer flask; about 10 cc. of 15 per cent potassium iodide solution are added to take care of all chlorine, both free and as hypochlorite, and the whole is then acidified with 5 cc. of a one in five solution of hydrochloric acid. The free iodine is now titrated with one-tenth normal thiosulphate solution. Calculate per cent of available chlorine.

ANALYSIS OF SALT.

Moisture.—The sample (10 grammes) is weighed into a perfectly dry Erlenmeyer flask (250 cc. capacity) covered by a small funnel, and heated on a sand bath at 140° to 150° Cent. for three to four hours. Water present as "moisture" will be driven off at this temperature. "Chemically combined" water, usually amounting to less than 0.1 per cent, is not driven off appreciably.

(NOTE—Final weighing should be made in a stoppered vessel.)

Foreign Matter, Not Including Ferric Oxide and Alumina.—A one gramme sample is dissolved in dilute hydrochloric acid and foreign matter separated by filtration and washing with hot water.

Ferric Oxide and Alumina.—The filtrate from "foreign matter" is then heated to boiling, sufficient

*From Paper, Report of the Committee on Sulphite Pulp read before the Technical Association of the Pulp and Paper Industry, at the annual meeting in New York, Feb. 17, 1916.

NH_4Cl is added to hold MgO in solution, and then NH_4OH until decidedly alkaline, boil, filter, wash with hot water until no reaction for chlorides is obtained; ignite over the blast or Meker and weigh as Fe_2O_3 and Al_2O_3 .

Calcium.—To this barely alkaline and boiling filtrate add excess ammonium oxalate slowly and allow to boil for several minutes. Filter, wash with hot water containing some ammonium oxalate and ignite the precipitated calcium oxalate (CaC_2O_4) to constant weight, and weigh as CaO ; or wash the CaC_2O_4 precipitate with hot H_2O , return to beaker, add H_2SO_4 (1.9), heat to 90° Cent. and titrate with KMnO_4 .

Magnesium.—To this filtrate, evaporated until crystallization of salts commences, add Na_2HPO_4 or ammonium phosphate; let stand fifteen minutes, add dilute NH_4OH equivalent to one-third the volume of the neutralized solution. Allow to stand in the cold, preferably in crushed ice, for several hours. Filter on alundum crucible, wash with cold ammonia (2 per cent; ignite at low heat, finally raising to the full heat of the Terrell burner, Meker burner, or blast. Weigh as $\text{Mg}_2\text{P}_2\text{O}_7$. Magnesium is considered as MgSO_4 , unless not enough SO_4 is present to saturate all CaO and MgO , when the remaining Mg is figured as MgCl_2 .

Sulphate.—A one gramme sample weighed into a small beaker and dissolved in dilute HCl is diluted to 100 cc. To the fairly acid and boiling solution, add slowly a 10 per cent solution of BaCl_2 until no further precipitate is obtained. Continue boiling for a few minutes and filter in an alundum crucible, washing with water almost at the boiling point until no chloride reaction is obtained with AgNO_3 . Ignite at full heat of the burner for several minutes and weigh as BaSO_4 . Sulphate obtained in excess of that required to satisfy CaO and MgO is considered as Na_2SO_4 .

Chloride.—Calculate to Cl . Dissolve 1 gramme in 100 cc. H_2O , filter off any insoluble residue, wash well, dilute to 200 cc., add a few drops of HNO_3 , heat to boiling, add excess of 10 per cent AgNO_3 solution; boil until coagulated, let stand a few minutes, or over night if convenient, filter on lundum or Gooch crucible, wash with hot water—return filtrate if not clear—dry one hour at 140 to 150° Cent., cool, and weigh as AgCl .

ANALYTICAL METHOD FOR LIME AND LIMESTONE.

Sampling.—Immediately after the car has been reported in at the acid plant, the laborer unloading the material should be instructed to reserve one shovelful from every third wheelbarrow when the car is unloaded. This pile is at once crushed, coned and quartered in the proper manner by a laboratory assistant, and a 1-quart mason jar filled, sealed and delivered to the laboratory. This sample should all pass a 5-mesh sieve.

NOTE.—This sample is further crushed, coned and quartered to several ounces of 50-mesh powder. For the analysis a further grinding in an agate mortar to 80-mesh powder will be sufficient.

Analysis of Silica and Insoluble Matter.—A one gramme sample is weighed into a small casserole, moistened with 10 cc. of water and decomposed by the addition of 5 to 10 cc. of a 1 in 2 solution of HCl and a few drops of HNO_3 , and the whole evaporated to dryness on a steam bath or low temperature electric hot plate. The dry residue is moistened with concentrated HCl , taken up with the least amount of water, heated to complete solution of soluble matter, and filtered. One washing of hot water is made, the filtrate and wash water are evaporated to dryness. (Omit dehydrating.) The dry residue is again taken up with HCl and hot water, boiled and filtered through the same paper, washed, and then ignited to constant weight.

Ferric and Aluminum Oxides (Fe_2O_3 , TiO_2 , etc.)—The filtrate from the silica determination (volume about 100 cc.) is treated with 5 cc. in excess of the amount of ammonium hydroxide (.90) necessary for complete precipitation, the solution boiled and the precipitate just dissolved by the addition of HCl . Ammonium hydroxide is then added in slight excess², the solution boiled until the odor of ammonia is just barely perceptible and filtered hot. The precipitate is washed well with hot water and ignited to constant weight. This figure gives the sum of Fe_2O_3 , Al_2O_3 , Mn_2O_3 , P_2O_5 , TiO_2 , etc.

NOTES.—(1) The dissolving of the first precipitate is necessary to produce sufficient NH_4Cl to hold the magnesium salts in solution; (2) the hydroxides may be dissolved and reprecipitated where a very accurate analysis is required, inasmuch as some calcium and magnesium salts may be included in the precipitate. For technical routine work this is hardly necessary.

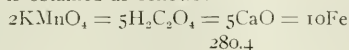
Calcium Oxide.—The combined filtrate (if a second precipitation is made) is boiled throughout the addition of a hot solution of ammonium oxalate plus a little ammonia, and the boiling continued for five minutes. The beaker is allowed to stand for one hour when the calcium oxalate should settle and filter readily. The precipitate is washed several times with hot water and dissolved with the smallest amount of a 1 in 2 solution of HCl , hot from the wash bottle, the solution being caught in the beaker in which the original precipitation was made. The filter is washed free from chlorides and a little ammonia solution poured over it. The solution is now made alkaline and several cc. of oxalate added, the whole boiled until the calcium oxalate settles readily, when it is filtered through a fresh paper and washed, not unnecessarily long, with hot water. This precipitate may be ignited and weighed as CaO or may be put into solution with sulphuric acid and the liberated oxalic acid titrated with standard permanganate as follows:

The precipitate of oxalate is rinsed off the paper into a 200 cc. beaker with hot water and the filter paper further thoroughly washed with hot dilute sulphuric

²Add bromine water, boil, adding more bromine water and ammonia if necessary to insure complete precipitation of the manganese.

acid. More sulphuric acid is added to the beaker and the whole is warmed until solution is complete. Titration is then made with standard permanganate solution.

NOTES—(1) The double precipitation of calcium is necessary to free the precipitate from small amounts of magnesia and alkali metals; (2) if the CaO is weighed as such, a check weighing is very important as the material is very hygroscopic and there should be as little delay as possible between the completion of ignition and weighing; (3) the permanganate solution is generally kept as a stock standard solution and its strength is known in terms of iron. If this is known, the iron value times .5016 equals the CaO value. This figure is obtained as follows:



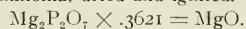
280.4

The ratio therefore $= \frac{5016}{280.4} = .5016$

559

Magnesium Oxide.—This determination is more difficult than any of the preceding, and strict adherence to directions is necessary.

Evaporate the combined filtrates from the CaO determination to a bulk of about 200 cc. and just acidify with HCl. Then add a considerable excess of microcosmic salt solution. The whole is then boiled for five minutes, cooled, and the excess acid carefully neutralized by the slow addition of dilute ammonium hydroxide with *constant stirring*. This is best accomplished by using a burette. When the precipitate appears, the addition of ammonia is stopped but the stirring is continued for some time. After about five minutes the solution is made strongly alkaline with ammonia (10 cc. conc.) and is allowed to stand over night. The precipitate should always be crystalline and easily filterable if this procedure is carefully followed. The precipitate is washed cold with 2 per cent ammonia, dried and ignited.



Alkali Metals.—If these are to be determined, which is very seldom the case, in a technical analysis, the method of J. Lawrence Smith should be followed. It is as accurate as any method and much more convenient.

Loss on Ignition.—Ignite a .5 gramme sample to constant weight over a blast lamp or large Meker burner. The loss gives CO₂ plus moisture, plus combined H₂O and organic matter.

Carbon Dioxide.—(NOTE—For the routine analysis of lime and limestone this determination may well be omitted.)—This determination is most easily made, especially on samples of lime, by means of an apparatus consisting of a small flask fitted with a two-hole stopper, through one hole of which a small dropping funnel is inserted, and through the other hole an outlet is made connecting with a small condenser. The condenser in turn discharges into a 100 cc. flask with a sufficiently large mouth to accommodate a small two-hole stopper. The second hole holds the mouth end of a 10 cc. pipette, which has the discharge end broken off

close to the enlarged portion, and this portion is filled with glass beads held in by a coil of wire placed in the lower end.

Ten cc. of 50 per cent KOH solution is placed in the 100 cc. flask, 1 gramme of the material and a small quantity of water in the boiling flask, hydrochloric acid in the funnel, and the apparatus is then connected up. The acid is run into the flask on the sample until sufficient is present to decompose the carbonate. The CO₂ distills over into the 100 cc. flask which forces the KOH up into the pipette until the gas bubbles through the beads. In this way the CO₂ is completely absorbed. The solution in the boiling flask is finally boiled for five minutes so that all CO₂ is driven from the apparatus into the receiver.

After distillation is completed, the pipette is partly removed from the receiver and thoroughly washed into the receiver. Water is added to make the volume 100 cc. in case of limestone and an aliquot part titrated with standard acid. In case of lime, the whole distillate may be titrated. The titration is carried to the disappearance of the red color with phenolphthalein and then to the appearance of the red color with methyl orange, the latter titration indicating the amount of carbon dioxide present.

ANALYSIS OF SULPHUR.

Sampling.—Portions are taken from a number of points throughout each car of sulphur received so as to give a fair average composition as compared with the carload as a whole. These portions are thoroughly crushed, mixed, quartered and, if necessary, quartered further until an amount of convenient size for a laboratory sample is obtained. This sample is placed in an airtight glass container and placed with similar samples from other carloads. These samples are preserved until a number equivalent to a "shipment" have been collected.

These samples are then thoroughly mixed and again sampled, ground to a 100-mesh powder and treated as follows:

NOTE.—Samples for moisture determination should not be ground too fine as moisture is lost in the grinding process.

Moisture.—For technical purposes, a 100-gramme sample, though not necessarily as fine as 100-mesh, is weighed into a glass-stoppered weighing bottle, dried first at 70° Cent. and finally at 100° Cent. for a short time. Evidences of sublimation should be noted and avoided. (Several hours in a vacuum desiccator would be better.)

Sulphur in Sulphur.—Two samples weighing one gramme each are weighed out into each of two extraction apparatus (Underwriters' Laboratory pattern) and subjected to the action of carbon disulphide for fifteen minutes. The sulphur itself is thereby dissolved from the small Gooch crucible leaving only the dirt and other impurities. The crucible is then removed from the apparatus, dried and weighed. Loss = S + moisture.

Ash.—A 10-gramme sample is weighed into a porcelain crucible or dish and carefully burned, the residue constituting the ash.

COAL ANALYSIS.

Coal Analysis.

As recommended in Technical Papers, No. 8 and No. 76 of the United States Bureau of Mines.

DAILY SOLUTIONS.

Tenth-normal sodium arsenite.

Tenth-normal iodine.

Hundredth-normal iodine.

Tenth-normal sodium hydroxide.

N/10 Sodium Arsenite.—Weigh out on a watch glass 4.05 grammes arsenous acid powder; transfer carefully to a liter beaker. Weigh out on a rough balance twenty grammes anhydrous sodium carbonate and add the arsenous acid. Fill beaker two-thirds full of water and put on a steam bath to dissolve. Finally cool to room temperature and make up to exactly 1,000 cc.

N/10 Iodine.—Made up from the normal solution which is prepared as follows for each liter: Weigh out on rough scales 162 grammes potassium iodide (free from iodate) in a beaker and add enough water to just cover. Then add 128 grammes of solid iodine flakes and stir, but do not heat to dissolve. When dissolved make up to one liter for use in the following solution:

Take 100 cc. of the above and make up to 1,000 cc. with water. Titrate against N/10 sodium arsenite, using starch as indicator, adding water or N/1 iodine, depending on whether the new solution proved to be stronger or weaker than tenth normal.

A convenient formula to use in this connection is here given. Use 20 cc. of the arsenite. When the new solution is found stronger than N/10 add

$$20 \times 1.000$$

—1,000=cc. water to add (per liter)

cc. iodine used

when too weak add

$$20 \times 100$$

100—

cc. iodine used

----- = cc. N/1 iodine to

9

add (per liter)

N/100 Iodine.—Take 100 cc. N/10 iodine and make up to 1,000 cc. Titrate against standard sodium arsenite (N/100), proceeding with corrections as above.

N/10 Sodium Hydroxide.—This solution, as in the case of the iodine, is made up from N/1 solution, prepared as follows, per liter:

Weigh out 122.5 grammes NaOH on rough balance. Dissolve in a one liter beaker and finally make up to one liter.

NOTE.—A normal NaOH solution contains 40 grammes NaOH per liter, hence weigh out about 45 grammes of electrolytic NaOH.

For the N/10 solution take 100 cc. of the N/1 and

make up to 1,000. Titrate against standard N/10 H_2SO_4 , using phenolphthalein as indicator, and adding water or N/1 NaOH when the solution is either too strong or too weak.

The rule of thumb method indicated for N/10 iodine is also applicable here.

If desired, make the iodine and caustic solutions sixteenth normal instead of tenth normal and use a 2 cc. sample. This gives percent free and total direct on the burette, when testing cooking acid, of course, neglecting specific gravity of the acid.

Solutions deteriorate rapidly and should be made up frequently. Where large quantities are used, they should be made up fresh each day.

TESTING COOKING ACID.

Testing Acid Calcium Bisulphite Solutions (Cooking Acid).—Many methods of testing cooking liquor have been proposed, some having the advantage of extreme brevity and low accuracy, others being more accurate, but too long and involved for technical purposes.

The method proposed is a mean between these two and while not giving strictly accurate results is quick and does give results accurate enough to furnish sufficient control over the manufacture and use of the cooking solution. It is the method used in a great many American sulphite mills.

One cc. of the acid, taken with a pipette, is diluted immediately by being placed in about 200 cc. clear cold water. Using starch solution as indicator, it is immediately titrated with tenth normal iodine.

A second cc. sample prepared as above is titrated with tenth normal caustic soda, using phenolphthalein as an indicator. Multiplying the cc. of iodine solution used by .0032 gives grammes SO_2 in one cc. of the cooking acid. Disregarding the specific gravity of the acid, this product is taken immediately as the total percent of SO_2 in the cooking acid.

In the same way is calculated the percent of free SO_2 .

Subtracting the percent *free* from the percent *total* gives the percent combined.

Dividing the percent *free* by the percent *total* gives the percent *free* of *total*.

The British vice-consul at Ekaterinburg, Russia, reports that the first cement works were opened in the Urals at Neviansk (Ekaterinburg-Perm Railway) during 1914. Formerly the Urals as well as the whole of western Siberia were dependent on cement transported from Russia from the Volga works at Saratof. The price of the Saratof cement used to be 80 kopecks per pood (\$22.82 per short ton at the normal exchange rate of \$0.515 to the ruble), and cement was scarce at this price. The cost of production at Neviansk, however, is stated to be about 2 rubles per barrel (\$5.15 per ton). The whole production of 500,000 barrels was sold during 1915. The quality of the cement, according to reports of the consumers, has proved satisfactory.

APPARATUS FOR DIGESTING AND INCINERATING CRUDE FIBER.*

By J. M. PICKEL.†

APPARATUS FOR DIGESTING CRUDE FIBER.

In an article¹ by the author several years ago, it was stated that round-bottom flasks, through which cold water is passing, set on the beakers in which crude fiber is digesting, prevent evaporation and hold frothing in check. The apparatus pictured here is the outgrowth of that idea. The distinctive feature of it is the round-bottom reflux condenser.

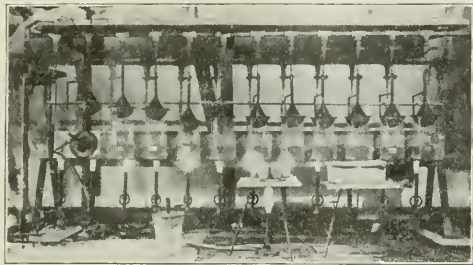


FIG. 1.

THE CONDENSERS.—In Fig. 1 eight of the condensers are shown resting on the beakers. Two are shown suspended above the beakers. One is suspended, giving a view of the tube, through which the cooling water passes out of the condenser. Another, lying on the heating plate, affords a top view. The parts of a condenser (see Fig. II) are: (a) a zinc or copper—in this case it chanced to be zinc—shell (hemisphere) 7.6 cm. in diameter; (b) a copper ring, similar to those used on water baths, about 10 cm. in diameter, the circular opening in the ring being about 5.7 cm. in diameter, this ring is soldered to the shell; (c) a copper cone whose big end is about 5.7 cm. in diameter, small end about 1 cm. in diameter (1.5 cm. would be better) and vertical height about 4.5 cm., this cone is soldered to the ring; (d) a copper tube about 1 cm. in diameter (1.5 cm. would be better) and about 11 cm. long, soldered to the cone; in the side of this tube near its top is a small hole, by means of which the condenser may be suspended on a catch or hook on the influx tube; (e) an elbow-shaped exit, or overflow, tube, about 4 mm. inside diameter (1 cm. would be better), length (horizontal) to the elbow about 7.5 cm., length (vertical) about 10 cm.; this tube is soldered to the tube (d) about 3.5 cm. above the cone.²

THE DELIVERY TUBES.—The cooling water is delivered into the condensers from the water-main by branch tubes each provided with a stop-cock. These cocks are ordinary brass gas-cocks, in the nozzles of

which are soldered copper tubes about 4 mm. inside diameter and 24 cm. long. The adjustment should be such that the lower ends of these tubes are about 4 mm. above the bottoms of the condensers when they are suspended and about 1 to 2 cm. below the top of the cone when the condensers rest on the beakers. The condensers are suspended from a little catch or hooks soldered to the delivery tubes. Whether the condensers be suspended above the beakers or be resting on them, the water circulates through them freely and spills into a trough back of the beakers—no rubber connections. A horizontal strip with holes in it, through which the overflow tubes pass, keeps the exit ends of these tubes centered over the trough. It is important that these ends should always be visible so that one may at any time know that there is ample flow of water through the condensers. These tubes should not, therefore, dip into the trough. The trough (galvanized sheet iron) is about 3.5 cm. wide, about 13 cm. deep and, of course, extends along the entire length of the "plant."

These condensers prevent completely loss of liquid by evaporation, and suppress, or hold sufficiently in check, frothing. But the boiling must be started gently and conducted gently; violent ebullition is not

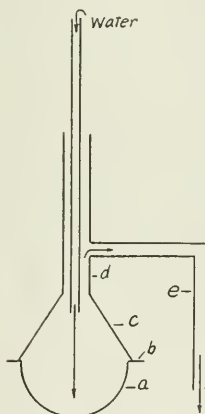


FIG. 2.

at all necessary and is to be avoided. Frothing is due to bubbles filled with steam—and doubtless to some extent with hot air; condense the steam and the bubbles or froth collapse. The upper region of the beakers is kept cool by the condensers; hence there is no need of a cold blast of air—it is the *coldness*, not the *blast*, that checks the frothing. A cold air-blast could, however, be easily introduced through these condensers. Such a condenser is shown on a beaker in the foreground of Fig. 1.

Beakers of 500 cc. capacity, 7.5 cm. inside diameter and 14 cm. high, Jena glass, are preferred; but beakers of 600 cc. capacity, 8 cm. diameter, 15.5 cm. high, can be used interchangeably with the smaller ones. The

*From Journal of Industrial and Engineering Chemistry.
¹Laboratory of North Carolina Department of Agriculture, Raleigh, N. C.
²Since writing the above, an ordinary glass flask, whose neck is provided with a suitable side-tube, has been used quite satisfactorily for several months instead of one of the metallic condensers.

beakers can be given a rotary shaking without lifting them from the heating plate. After the boiling has been gotten under way and the beakers have been rotated a time or two, the apparatus may be left to itself,

The heating plate (wrought iron) is about 4 mm. thick and has a top surface about 9.5 cm. wide. Along its entire length is turned a flange about 2.5 cm. wide. The object of the flange is to give rigidity and prevent sagging or buckling.

A FURNACE FOR CRUDE FIBER INCINERATION.

If the chemist have at his disposal the requisite electric current and \$50 to \$100, he will be apt to invest in an electric furnace. If he have but a dollar or two, he can, with that capital and with materials ready to hand in the laboratory, construct a wonderfully efficient incinerating furnace. Such a furnace, occupying on the table a space 20×20 cm. (8×8 in.), is shown in Fig. 1, at the left uncovered, at the right as it appears when performing. Twelve crude fiber incinerations are made in 15 to 20 min. on, or in, this furnace by the heat of one small Bunsen burner; and the ash is as nearly perfect as the writer and designer of the furnace has ever seen.

A piece of asbestos board 0.7×19×19 cm., in whose center is cut a circular opening 9 cm. in diameter, is laid on an ordinary laboratory tripod. On this board is set a disc of wrought iron (cast iron would probably be better) about 2.5 mm. thick and 13.5 cm. in diameter (14.5 cm. would be better since it would furnish space for several more incinerations). The disc is supported on three legs, 1 cm. long, screwed into it. On the disc are set 12 crucibles, alundum RA 98, 3.8 cm. high and 3.7 cm. in outside diameter, in which the fiber has been filtered, washed, dried and weighed. On the asbestos board is placed an asbestos cylinder 15.5 cm. in diameter and 6.5 cm. deep. The cylinder is covered with a piece of asbestos board of the same dimensions as the one previously described, but having in its center a hole only 3.5 cm. in diameter. A small Bunsen burner, whose gas tip has been widened somewhat by inserting the point of a pen-knife blade, furnishes the heat. The burner should be set on a block so as to bring its top close to the iron disc, thus causing the flame to spread over the under surface of the disc. In a few minutes (6 or 8) the disc and the crucibles will be brought to a bright glow.

The cylinder is easily and quickly made. Strips of suitable width (about 6.5 cm.) are cut from asbestos board of suitable thickness (about 7 mm.) and their ends beveled by shaving with a sharp knife. These strips are saturated with water, and, while wet, are wound, two or three thicknesses, around a suitable core (an empty 2-kilo ether can or a piece of sheet-iron stovepipe), bound in place by two or three bands of wire and allowed to dry out at room temperature and finally on or near a steam radiator. The core is removed and the lapped ends of the strips riveted.

A SIMPLE VACUUM DISTILLING APPARATUS.*

By T. G. GREAVES.†

A vacuum distilling apparatus is frequently used in laboratories for concentrating liquids or distilling at as low a temperature or as rapidly as possible. It was recently found to be difficult to replace parts or get a new unit because of war conditions, so a simpler form was devised, which is also more satisfactory, because it eliminates a joint with a rubber ring which experience has shown is liable to leak and affect the reduction of pressure.

The apparatus listed in the catalogues at \$7.00 to \$7.50, without thermometer or water bath, consists of a heavy, flat porcelain dish made to fit into a pan (water bath) and a glass dome which rests on a rubber ring which is the packing of the joint between the dish and the dome. The top of the dome has a ground opening into which fits a tube which has a side branch to convey vapor to the condenser and the top of which has a rubber stopper with a hole for a thermometer.

In place of this we are now using a glass gallon whisky jug, which costs 10 cents, with a rubber stopper carrying a bent tube to convey vapor to the condenser and a smaller hole which can be used for a thermometer. A thermometer is not used, however, as the vacuum gauge gives the approximate temperature, but in place of it a bent tube which connects by a rubber tube with a supply of the liquor so that the apparatus may be refilled by opening a pinch cock, without breaking the vacuum. The jug is placed in a sauce pan of water with pieces of metal or glass tubing in the bottom to keep it from being cracked by boiling the water. The diameter of the jug is the same as that of the German apparatus. It holds the maximum vacuum uniformly without watching. It can be adjusted so that the liquid drips into it constantly.

A geologic reconnaissance for phosphate in the Salt River Range of Wyoming, by G. R. Mansfield, of the United States Geological Survey, has resulted in a brief report showing the location and character of beds of rock phosphate of medium grade on the west flank of that range. This investigation is part of the exploratory work and mapping which the Geological Survey is doing in the western phosphate field. This work has already resulted in the discovery of beds of phosphate, most of it of high grade, aggregating several billion tons. The present report is designated as Bulletin 620-O and may be had on application to the Director, Geological Survey, Washington, D. C.

*From Journal Leather Chemists' Association.

†Laboratory of John H. Heald & Co., Inc., Lynchburg, Va.

METALLURGY

DETERMINATION OF CARBON IN STEELS AND IRONS BY DIRECT COMBUSTION IN OXYGEN AT HIGH TEMPERATURES.*

By J. R. CAIN, Associate Chemist, and H. E. CLEAVES, Assistant Chemist.

The influence of temperature on the results obtained by the direct combustion of steel and iron in oxygen has been frequently investigated¹ and the general consensus of opinion seems to be that higher results for carbon are obtained with higher combustion temperatures. This conclusion, however, is rendered doubtful by a number of circumstances: (1) Quite frequently, because of uncertainties in blanks it is impossible to conclude whether the difference in results claimed is due to variation in blank or is real; (2) the published work does not indicate that investigators have always assured themselves that the material used to support the drillings or that the fluxes sometimes used are completely free from carbon; (3) differences in carbon results with the same steel are frequently due to a variation in the size of drillings used.

Combustions of steel are ordinarily made in such a way that the oxides are in the fused condition for only a very short time. This is evident from work done here, which shows that the fusion point of the oxides themselves is above 1450°,² and that as soon as the fused material has combined with or permeated the bed material the melting point of the combination becomes much higher. The temperature of a combustion furnace as ordinarily operated does not exceed 1200° and usually lies between 950° and 1100°, hence it is evident that the oxides from 1 or 2 grams of steel must solidify very rapidly after the combustion period is over, for it is only during this time that the temperature is above the melting point of the oxides. Burning in the ordinary way, if the sample consists of very large particles there is always the danger of incomplete combustion of all its parts; on the other hand, if the particles are very small the combustion may proceed so rapidly as to cause initial fusion of a portion of the oxides followed by quick solidification of the fused part with resultant inclosure of yet unburned metal. There is some chance, too, that carbon dioxide or monoxide may be inclosed in the solidified mass, and that with certain alloy steels difficult oxidizable carbides (silicon, tungsten, chromium)

may escape oxidation except at very high temperatures.

A consideration of these facts, together with previous experimental work here and elsewhere, which showed that oxides from apparently well-burned samples yielded additional carbon upon being finely pulverized and reburned, led to the development of the present method, in which the sources of error cited in the first paragraph are eliminated. The object of this work was to develop a procedure which would give the best possible chance for oxidation and liberation of all the carbon in the sample, regardless of the original size of drillings, and especially to ascertain by such method the order of the error, if any, which affected the carbon determinations reported on the certificates for the Bureau's series of standard analyzed irons and steels. The latter determinations were made as usual either by direct combustion of the metal at temperatures of 950° to 1200°, or else by burning the carbon residue left after solution of the steel or iron in a suitable solvent.³ Briefly, our method consisted in burning the metal directly in oxygen within the usual temperature range, then raising the temperature to a point above the fusion point of the oxides and maintaining this temperature long enough to insure that all parts of the sample had been brought in contact with oxygen or fused iron oxide. The sample was burned directly on platinum (with precautions described later), so that no carbon could be obtained from the support for the drillings; the carbon was estimated by the barium carbonate titration method devised by one of the authors⁴ and in such way that the blank was negligible.

It seemed first desirable to know whether carbon dioxide or monoxide were left inclosed in the oxides produced during the direct combustion process as ordinarily carried out. To determine this there was used an apparatus consisting of an evolution flask connected to a suitable purifying train followed by absorption tubes for carbon dioxide and monoxide.⁵ In the evolution flask there was placed a large excess of concentrated hydrochloric acid together with the uncrushed oxides resulting from the combustion in the ordinary way (on pure alundum) of twenty-two 2-gram samples of steels known to yield carbon upon reburning after pulverizing. Boiling the contents of the flask for several hours resulted in complete solution of everything except the mechanically held alundum, and during this time a current of air purified

*From Technologic Paper of Bureau of Standards. This paper is an amplification of a preliminary paper on this subject by the same authors. See J. Wash. Acad. Sci., 4, p. 393; 1914.

¹See Lorenz, Z. Angew. Chem., 5, pp. 315, 395, 411, 435; and Foerster, Z. Anorg. Chem., 8, p. 274, 1895, for work at high temperatures; for references to work at other temperatures, see article by Mueller and Diethelm, Z. Angew. Chem., 27, p. 2114; 1910.

²By G. K. Burgess and R. G. Waltenburg, unpublished.

³In a few cases certificate results include the carbon obtained from reburning the oxides.

⁴J. R. Cain, B. S. Tech. Paper No. 33; J. Ind. and Eng. Chem., 6, p. 465; 1914.

⁵With palladium chloride and iodine pentoxide tubes were used.

from carbon dioxide and monoxide was passed through the apparatus. The carbon dioxide found in the absorption tube was 0.00104 gram, which would correspond to 0.0007 per cent carbon on the basis of 44 grams of metal taken; the absorption tube for carbon monoxide showed none of this gas to be present. It seems fair to conclude from this experiment that any error in ordinary combustions resulting from occlusion or inclusion of carbon dioxide or monoxide is quite negligible. The case might be different where silica is used as supporting material for drillings, and there is consequently the possibility of forming viscous, slowly solidifying slags which might well retain large bubbles of gas. It should be noted in this connection that immediately after the combustion of metal has ceased the partial pressure of carbon dioxide and monoxide inside the combustion tube reaches a maximum because the incoming oxygen has been almost completely consumed by the metal, leaving but little excess to sweep on the products of combustion; the

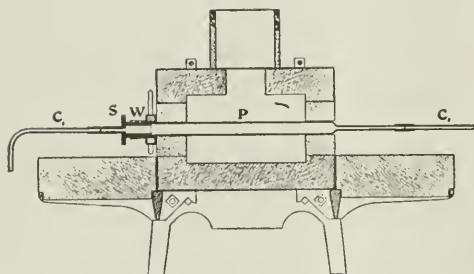


Fig. 1.—Cross Section of Gas Furnace.

C₁, C₂, Copper tubes soldered to platinum tube. S, German silver stopper. W, Water jacket.

oxides begin to freeze very soon after, and accordingly conditions are then very favorable for retention of carbon dioxide or monoxide by the solidifying oxides. However, as stated, when nonviscous, quickly solidifying oxides result, as in our experiment, the error from this cause may be regarded as negligible.

For carrying out combustions under the conditions selected by us—initial temperatures of 1050° to 1100° followed by temperatures above 1450° and burning the metal directly supported on platinum—it was necessary either to start with low temperatures and slow oxygen current, increasing both as the skin of oxide on the grains became thick enough to protect the platinum, or else to burn initially in a furnace kept at the lower temperatures and then transfer the boat and contents to the high-temperature furnace. The first method was carried out in the gas furnace shown in Figs 1 and 2;⁶ the second procedure was used with our usual nichrome-wound furnaces in conjunction with the platinum-wound furnace shown in Fig. 3. In view of the failure to find notably higher results by our method (as will appear later), we did not deem it

worth while to proceed to the next obvious step in apparatus—the construction of a single electric furnace suitable for both stages of the combustion. The electric-furnace method is very much to be preferred. The required temperatures are reached and maintained with much greater regularity and convenience than when gas is used, the wear on the platinum is less, and the chance for error from extraneous carbon dioxide is eliminated. The gas furnace is very destructive in

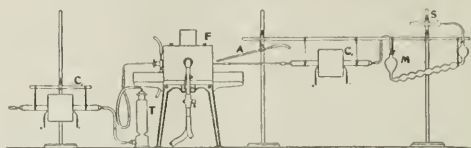


Fig. 2.—Apparatus for High Temperature Combustion.

A, Air cooling tube. C₁, C₂, Copper oxide catalyzers. F, Gas furnace shown in Fig. 1. M, Meyer tube. S, Soda lime tube. T, Caustic potash jar.

its effects on the combustion tube, but the boats seem to suffer very little by either method. If, however, the operation of the gas furnace is conducted carelessly, so that the temperature initially is caused to rise too rapidly and the fusion temperature of the oxides is reached before all the iron is burned, then a boat is soon destroyed by alloying with iron; this is also the case if the combustion of metal is incomplete in the first electric furnace when using that method. Temperatures were measured with a Wanner optical pyrometer and with a platinum-iridium thermo-element in conjunction with a millivoltmeter. The low-temperature electric furnace was maintained at 1050° to 1100°, the high-temperature electric furnace at 1475°; the gas furnace was started from room temperature and raised gradually to 1525°, at which temperature it was held during the fusion period. The copper

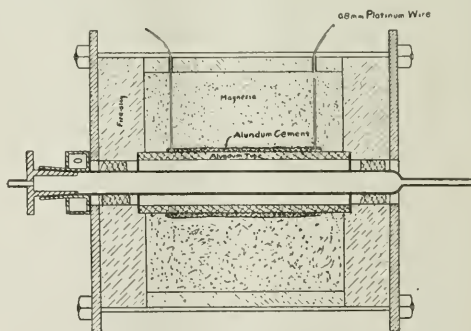


Fig. 3.—Electric Furnace for High Temperature Combustion.

oxide catalyzer following the furnace was found absolutely necessary when using the gas furnace, otherwise very large amounts of carbon monoxide were produced and escaped absorption; the low-temperature electric furnace also contained heated copper oxide in the forward portion of the (porcelain) combustion tube.

⁶Reproduced from our first paper on high temperature carbon combustions, above cited.

The routine followed in making a determination in the gas furnace consisted in inserting into the combustion tube the boat holding the sample and connecting up the Meyer tube containing barium hydroxide solution. While passing a slow current of oxygen the combustion tube was brought to 700° or 800° and kept within these temperatures for a minute or two until the superficial oxidation of the particles was effected; then the temperature was raised to 1050° or 1100° and the combustion of the iron completed. As soon as absorption of oxygen by the burning metal had ceased the blowpipe flame was turned on full, this stage of the combustion being continued 25 to 30 minutes. The Meyer tube was disconnected and the determination finished by filtering off and washing the precipitated barium carbonate and titrating it against standard acid as described in the cited paper on this method. The procedure when using the electric-furnace method was to place the boat containing the sample in the already heated nichrome furnace, starting with a very slow current of oxygen, increasing gradually to the rate usually maintained and holding this condition until all the metal was burned and the carbon dioxide swept out the combustion tube. Then the connection of the Meyer tube was changed to the near-by high-temperature furnace through which oxygen was passing and the boat was transferred quickly to this furnace, which was maintained continuously at the proper temperature. After remaining in the high-temperature furnace 15 to 20 minutes the Meyer tube was disconnected and the filtration and titration finished as before. The oxides were usually found to be thoroughly fused and to have spread over the bottom of the boat; in some cases they even crept over the sides of the container. A second fusion of such oxides gave no further carbon dioxide to a freshly filled and clear barium hydroxide tube.

Great care was taken at all stages of the work to eliminate extraneous carbon dioxide or other substances that would cause a blank, so that, as already stated, the blank was always negligible. The frequent blanks which were made during this work were carried out (1) without any steel in the furnace; (2) when burning Bureau of Standards standard steel No. 23, which, as shown in the table of results in this paper, gives identical values when burned in the ordinary way and by our modified method. The fused oxides were readily removed from the boats, in preparation for the next combustion, by digesting in strong hydrochloric acid for a few hours.

The results show that some steels give higher results by the new method than are shown on the certificates, others yield only slightly higher figures, and still others give the same results by both methods. We find it impossible to relate these three classes with the size of drillings used, with the carbon content of the sample, or especially, with the presence or absence of the usual alloying elements. In only two cases were the results by the modified method as much as

0.02 per cent higher than the certificate value; with most of the other samples the difference was of the order of 0.01 per cent. Our work does not cover the Bureau's complete series of standard analyzed steels and irons, but the results are deemed quite representative, and we believe they are complete enough to justify us in the conclusion that the certificate values for these steels cannot be affected with an error greater than 0.015 per cent (probably minus), and in most cases the error is much less. It is believed that such errors are negligible, considering the uses to which these standards are at present being put.

TABLE 1.—RESULTS ON BUREAU OF STANDARDS STANDARD IRONS AND STEELS.

Description and Bureau of Standards number of sample.	Certificate value for carbon—average of all methods.	Results obtained by combustion at high temperatures—average values.	Difference (average values—certificate values).
Bessemer:			
0.1 per cent C, No. 8a.....	0.084	0.087	+0.003
0.4 per cent C, No. 10b.....	.373*	.372	— .001
0.8 per cent C, No. 23.....	.805	.805	— .000
B. O. H.:			
0.1 per cent C, No. 15a.....	.111	.117	+ .006
0.4 per cent C, No. 12a.....	.364	.378	+ .014
0.8 per cent C, No. 14a.....	.815	.816	+ .001
A. O. H.:			
0.2 per cent C, No. 19a.....	.207	.216	+ .009
0.6 per cent C, No. 21.....	.591	.600	+ .009
1 per cent C, No. 35.....	1.03	1.05	+0.02
Alloy steels:			
Chrome vanadium, No. 3.....	.373	.379	+ .006
Chrome nickel, No. 32.....	.372	.383	+ .011
Chrome tungsten, No. 31.....	.599	.609	+ .010
Nickel steel, No. 33.....	.278	.285	+ .007
Vanadium steel, No. 24.....	.348	.352	+ .004
Irons:			
Iron C, No. 5b.....	2.726	2.743	+ .017
Iron D, No. 6a.....	2.46	2.48	+ .02

*Certificate value, direct combustion, 0.363.

The experimental difficulties and the inconvenience of this method of determining carbon place it beyond the reach of most industrial and works laboratories, and we do not, therefore, recommend its use to such, except in the case of products for which it may be found better adapted than other methods.

The U. S. consul at Breslau, Germany, reports under date of March 17 that on account of the rising tendency of the cost of raw material the paper factories for technical purposes have raised prices, as follows: Tracing paper, 20 per cent; oil paper, 40 per cent; drawing paper, 30 per cent; copying paper, 50 per cent; and carbon paper, 50 per cent in addition to the recent increase of 30 per cent. The Normal Paper Convention has raised the prices for normal paper by 20 per cent, to be effective at once. The grades 4a and 4b are especially wanted by the authorities. The Pergamyn Convention, which lately raised prices by \$0.016 per pound, is about to declare a further increase.

A NEW METHOD FOR DETERMINATION OF GASES IN STEEL.*

A new method for the determination of gases in steel by Goerens and Paquet is described in *Stahl und Eisen*, and some results are given. This method aims to obviate the chief defects of previous ones, and consists in melting the steel to be examined in a vacuum with tin and antimony, and determining the gases set free. An electric resistance furnace is used for melting, and a magnesia crucible previously heated to a high temperature and made free from gases.

The apparatus used for analyzing the gases is similar to the well-known Orsat. Special attention should be directed to the obtaining of clean drillings, for naturally this is very important, and due to the irregular distribution of gases in steel drillings should be taken through the whole section. Three grams are melted with 3 grams of gas-free tin (Kahlbaum) and 3 grams gas-free antimony (also Kahlbaum). The mixture is heated high enough so that the whole is uniformly liquid, which takes place when the built-in pyrometer registers 1,100 deg. C. The time for a test, including the analysis of the gases, usually takes three hours. When working with the same material the results obtained lie within the allowable limits of experimental error.

In the table are given results obtained on rolled and forged samples of many kinds of steel. They are arranged according to increasing gas contents. A good measure is the total number of cubic centimeters per 100 grams of steel. The lowest result was

obtained with a low carbon electric steel, and such well deoxidized steel has 10 to 15 c.c. per 100 gr. metal. High carbon electric steel in general contains more gas, but the amounts are not proportional to the carbon. Low carbon basic-Bessemer and open-hearth steel show average amounts, 22 to 78 c.c. per 100 gr. A comparatively high gas content, strangely enough, was found in a crucible steel, 152 c.c. per 100 gr., but this result cannot be taken as standard because the steel tested was admittedly defective.

The carbon dioxide varies from 0.002 to 0.02 per cent by weight. The amount of this gas found depends to some extent on the way in which the determination is carried out, so the figures given do not allow definite conclusions to be drawn. The carbon monoxide also varies within wide limits, from 0.0015 to over 0.1 per cent. A high carbon monoxide content is generally a proof that the deoxidation was not complete. In the case of the carefully made chromenickel steel, No. 9 in the table, for example, the carbon monoxide, CO, was only 0.0015 per cent. Also the addition of ferrosilicon, which serves to alleviate the formation of carbon monoxide during deoxidation, does not insure a gas-free or carbon-monoxide-free material, as may be seen from samples 18, 21 and 26 in the table.

The hydrogen varies from 0.0002 to 0.0047 per cent. Carefully prepared and well deoxidized low-carbon steel contains little hydrogen as a rule; often its amount depends to a large extent on the charge. The nitrogen varies from nothing to 0.0141 per cent, but as it was determined by difference, and therefore car-

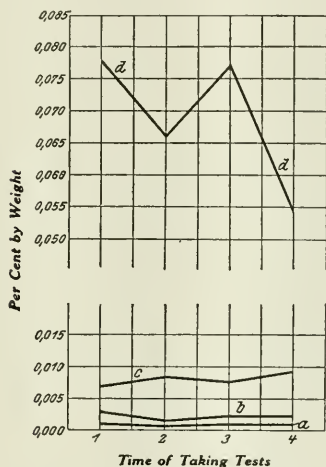
*From The Iron Age.

TABLE OF GAS CONTENTS OF VARIOUS STEELS.

Test No.	Analysis						Gas per 100 g. Ma-	Per Cent by Weight					
	Carbon, Pct.	Manganese, Pct.	Phosphorus, Pct.	Sulphur, Pct.	Silicon, Pct.	Nickel, Pct.	terial cc.	CO ₂ .	CO.	H.	N.	Total.	
(a) Low Carbon Basic Bessemer.													
1.....	0.05	0.36	0.11	0.045	...	...	22	0.0040	0.0196	0.0003	0.0029	0.0268	
2.....	0.08	0.40	0.08	0.048	...	...	40	0.0090	0.0352	0.0006	0.0025	0.0383	
3.....	0.05	?	0.08	0.040	...	...	41	0.0077	0.0342	0.0006	0.0005	0.0413	
4.....	0.05	0.40	0.08	0.040	...	...	49	0.0061	0.0393	0.0006	0.0122	0.0521	
(b) Low Carbon Open Hearth.													
5.....	0.08	0.40	0.05	0.030	...	...	38	0.0048	0.0341	0.0005	0.0061	0.0455	
6.....	0.15	0.37	0.06	0.060	...	...	46	0.0048	0.0410	0.0009	0.0024	0.0443	
7.....	0.08	0.44	0.04	0.037	...	...	78	0.0178	0.0785	0.0007	0.0020	0.0812	
(c) Electric Steel.													
8.....	0.19	0.50	0.020	0.012	0.42	...	10	0.0047	0.0061	0.0002	0.0015	0.0125	
9.....	0.08	0.35	0.010	0.010	0.09	4.34	1.10	13	0.0082	0.0015	0.0007	0.0000	0.0104
10.....	0.10	0.38	0.011	0.010	0.07	3.30	...	15	0.0064	0.0061	0.0007	0.0000	0.0132
11.....	0.15	0.49	0.011	0.012	0.45	...	...	25	0.0058	0.0092	0.0012	0.0048	0.0210
12.....	0.26	0.43	0.068	0.023	0.015	...	...	25	0.0053	0.0098	0.0012	0.0041	0.0214
13.....	0.10	0.40	0.010	0.012	0.10	...	...	28	0.0053	0.0207	0.0008	0.0019	0.0287
14.....	0.45	0.38	0.018	0.022	1.27	...	...	32	0.0058	0.0167	0.0013	0.0042	0.0280
15.....	0.98	0.45	0.158	0.075	0.015	...	...	70	0.0043	0.0688	0.0010	0.0083	0.0824
16.....	0.71	0.37	0.018	0.016	0.23	...	...	73	0.0106	0.0684	0.0010	0.0078	0.0878
17.....	1.35	0.44	0.020	0.015	0.19	...	0.37	88	0.0053	0.0851	0.0010	0.0141	0.1055
18.....	0.10	0.35	0.009	0.008	0.17	3.62	0.90	94	0.0018	0.0569	0.0047	0.0012	0.0646
19.....	1.16	0.38	0.017	0.016	0.18	...	...	94	0.0050	0.0900	0.0011	0.0124	0.1085
20.....	0.33	0.38	0.026	0.016	0.10	3.06	1.94	105	0.0109	0.0708	0.0039	0.0056	0.0912
(d) Crucible Steel.													
						Ni.	Wo.						
21.....	0.38	0.26	0.056	0.021	0.19	...	0.65	29	0.0090	0.0248	0.0004	0.0024	0.0366
22.....	0.84	0.36	0.011	0.017	0.15	...	...	41	0.0058	0.0391	0.0007	0.0015	0.0471
(e) Crucible Steel.													
						Cr.							
23.....	0.16	0.44	0.008	0.008	0.29	4.0	0.91	50	0.0032	0.0271	0.0022	0.0053	0.0378
24.....	0.47	...	0.020	0.028	...	2.98	1.29	51	0.0200	0.0257	0.0016	0.0068	0.0541
25.....	0.97	0.14	...	0.010	0.12	...	...	79	0.0098	0.0712	0.0017	0.0020	0.0847
26.....	0.27	0.45	0.010	0.012	0.24	4.0	1.30	152	0.0096	0.1290	0.0041	0.0082	0.1509

ries all the errors of determination of the other gases, very careful tests will still have to be made before any further can be said.

Tests were also made at various stages of the basic Bessemer and open-hearth processes. With the former four tests were taken from two heats, test 1 immediately before the deoxidation, test 2 while casting the first ingots, test 3 while casting the sixth ingots, and test 4 of the rolled material. The carbon monoxide shows the most important changes, 0.01 per cent in test 1, 0.059 in test 2. During pouring there is a slight decrease showing that in this time there is a constant action between the oxides and the carbon monoxide. During the stay in the soaking pits and during rolling, further amounts of gas escape, so that after the roll-



Gas Curves with Open Hearth Process.

1, After melting. 2, Before deoxidation. 3, After deoxidation. 4, After rolling. a, Hydrogen. b, Nitrogen. c, Carbon dioxide. d, Carbon monoxide.

ing the CO has dropped to 0.025 per cent, which is still higher than before the deoxidation.

The results with the open-hearth tests are shown in the illustration which gives the average of two heats. Test 1 was taken when the bath was clear melted, test 2 immediately before deoxidation, test 3 while pouring the first ingots and test 4 from the rolled material. The important difference between the two processes is that at the end of the operation before deoxidation the Bessemer metal contains very little, but the open-hearth considerable gas, probably because the nitrogen blowing through the metal carries the carbonmonoxide with it.

The results with the electric furnace process show the possibility of obtaining very low percentage of gases if sufficient time and care is taken. Not enough tests have been made, however, to compare the different processes.

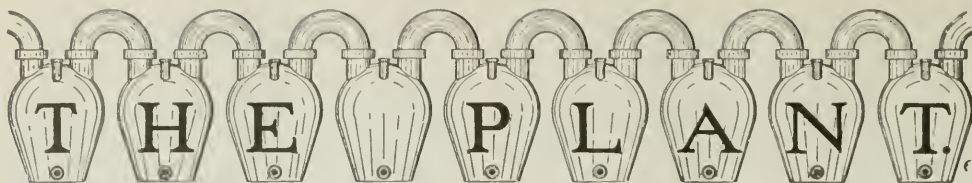
NEW CHEMICAL COMPANIES GET JAPANESE SUBSIDIES.

Japan's offer of subsidies for the manufacture of dyes and chemicals has resulted in the formation of three companies in addition to the dyestuff concern already reported. The Hongkong Daily Press quotes the British commercial attache as giving the details of their formation. One company, engaged in the manufacture of glycerin, with a capital of 3,000,000 yen (\$1,494,000), intends to take over the business of an oil company at Osaka. The second company, manufacturing medicinal and chemical products, intends to specialize in the manufacture of formalin and its derivatives and in other carbon compounds. This company will have a capital of 500,000 yen (\$240,000) and will acquire the formalin works of an existing Japanese concern engaged in the production of acetic acid. The third company produces medicinal compounds and will have a capital of 1,000,000 yen (\$498,000).

The promoters of such subsidized companies are required in the case of chemicals to apply to the Minister of Agriculture and Commerce for permission, and in the case of drugs to the Minister for Home Affairs. When part of the capital is paid up, the first general meeting of the shareholders completed, and the new company registered in the courts, the promoters are entitled to ask for a subsidy. This is to be available for not more than 10 years from the date of the enforcement of the law. The amount to be paid by the government is to be such as to make the dividends the company pays in each business year reach a rate of 8 per cent on the paid-up shares.

THE ALCOHOL MILK TEST.

The alcohol milk test, used to some extent in Europe and believed by some investigators to be a quick means of testing the condition and keeping quality of milk, is not a satisfactory substitute for bacterial examination, according to bacteriologists of the United States Department of Agriculture. The alcohol test is based on the fact that when equal parts of 68 per cent alcohol and milk are mixed and the mixture shaken gently in a test tube a flaky, white precipitate will form under certain conditions. The occurrence of this precipitate is held, by those who believe in the test, to indicate that changes have been produced in mixed market milk as a result of bacterial fermentation. The department's investigators who have reported on the results of this test in bulletin 202, "The Alcohol Test in Relation to Milk," however, find that alcohol will produce this precipitate when the mixed market milk contains a certain amount of lactic acid or rennet produced by varieties of bacteria which form these substances. As a consequence, milk may be high in bacteria of other varieties without showing the precipitate when alcohol is added.



THE MANUFACTURE OF PAPER PULP FROM STRAW.*

One of the most satisfactory accounts of the manufacturing operations involved in the cooking of straw for pulp was contained in a paper by James Beveridge, read some time ago before the Society of Chemical Industry. The availability of straw as a source of pulp is again receiving consideration owing to the increasing scarcity of the papermaking materials ordinarily used. This is particularly true as regards paper mills in England, where it is deemed possible, according to *Paper Making* (from which we take extracts from Mr. Beveridge's paper), that the increasing difficulty of obtaining raw materials may lead to a more general use of straw.

There are two kinds of pulp made from straw—viz., strawpulp proper, and what may be more correctly termed straw cellulose. The former is made by steeping the straw or boiling it under pressure with milk of lime until it is thoroughly softened, after which it is washed and ground with suitable machinery and manufactured into a cheap quality of wrapping paper. This method is employed extensively in France and other countries of the Continent where there is a demand for such papers, but is not used in England to any great extent, excepting probably in the manufacture of strawboards.

Although the subject of this paper has nothing to do with this kind of strawpulp, yet it may be mentioned incidentally that the chemical action of the milk of lime on the incrusting materials surrounding the straw fiber is not a vigorous one. These incrusting materials are not completely nor, indeed, to a great extent separated from the cellulose. The mineral matter remains in the product practically untouched, and if any less quantity than that corresponding to the percentage in the original straw operated upon exists in the prepared pulp, it is due rather to the washing after digesting than to any solvent action of the milk of lime. The milk of lime, under certain conditions, has a bleaching action on the straw. It neutralizes the organic acids usually formed when fibrous plants are heated for any length of time in presence of water.

The yield of pulp obtained by such a treatment amounts to from 75 to 85 per cent. The papers produced from this pulp are of a very poor quality, and wholly used for packing purposes. They are hard, brittle, and possess a low tensile strength. The preparation of pure cellulose from straw is a very differ-

ent manufacture, and involves a cycle of operations, each of which requires the most careful supervision. The product is used for the production of papers of first-class quality, fine and medium writings, for example, and must be well prepared, and as free from dirt as it is possible to get it. It is, therefore, necessary that cleanliness be observed in every department and that the straw itself and the water used for washing are subjected to a preliminary purification as necessity may require before they enter the mill.

The straws usually employed for the preparation of cellulose are those obtained from the cereals, oat, wheat, rye, and barley. In some parts of the Continent maize straw has also been used, but with only moderate success, as it yields a somewhat coarse fiber. Next to wood, oat, wheat, rye, and barley straws are the most universally distributed fibrous plants known as sources of paper pulp. In point of cheapness they also rank next to wood, which is recognized as the cheapest source of cellulose at present known in this country. The physical character and composition, especially with regard to their ash contents, vary enormously. This is true not only of the different kinds of straw, but also of the same variety, and seems to depend upon the district or country in which they are grown. Probably the soil has influences on the composition of the ash as well.

The fibers contained in the straws are loosely bound together by resinous and intercellular matter, which is easily dissolved by caustic soda, and subsequently separated by washing. Thus isolated they are soft, flocculent, and admirably adapted for use in the manufacture of high class writing papers. They differ slightly from one another in their papermaking qualities; the fibers from barley straw, for example, differing from those of oat, wheat and rye in length, breadth, and general physical character. This difference is very noticeable when the pulp from each of these straws is separately brought forward in the mill. It is not very difficult to classify the straws according to the nature of the fiber or cellulose they yield, although such a classification is true only locally. As regards Dutch straws, the following bears directly on them: Barley straw yields a very short fiber of low felting power. The knots and husks are soft, and in consequence this kind of straw is easily digested. Oat straw is usually somewhat harder; the knots and husks are more difficult to digest. The fibers it yields are comparatively long, soft, and of medium felting power.

*From Paper.

Wheat and straw are closely allied. They both yield long fibers of good felting power and are the most valuable as sources of cellulose. Rye straw in particular yields cellulose of excellent quality, and as it usually contains a comparatively small quantity of mineral matter, it is soft and easily digested.

MANUFACTURING OPERATIONS.

Cleaning.—The straw, as it is brought from the stacks or storehouse, is first of all passed through a machine to open it thoroughly, or this may be done by hand. It is then delivered or placed upon tables made of wire gauze, one-quarter inch meshes, alongside of which girls stand, whose duty it is to remove all weeds and other plants likely to produce what is known as shive in the finished pulp. From these tables it is elevated either automatically or by hand to the cutter, which usually consists of the ordinary chaff cutter used by farmers. The straw is fed continuously by an endless traveling belt through an orifice, across the face of which at right angles to the feed a wheel revolves, having one or more knives attached to its spokes. The length of cut varies from half an inch to one and a half inches. From this the chaff falls on an inclined jogging sieve of one-eighth inch wire gauze, and in traveling to the lower end the bulk of the sand, husks and fruit grains are separated. Although the chaff at this stage is tolerably well cleaned, some manufacturers prefer to give it a final sifting, and to do this they employ a revolving sieve, through the center of which a shaft revolves at a high velocity. This shaft has pegs studded along its length at equal intervals, and so placed as to form a kind of archimedean screw. The sieve is cone-shaped or slightly inclined, and as the chaff travels forward all loose dirt is separated, being carried through the meshes by the current of air induced by the revolving shaft. It is then stored in heaps ready for the pulp boilers.

The object in subjecting the straw to such a trenchant system of cleaning as above indicated is to remove all foreign weeds, husks, fruit grains and sand. This is absolutely necessary for the production of high-class pulp, for it has been found by experience that these impurities produce more or less unbleachable particles, and much of the success attained in avoiding these imperfections depends on the completeness and care with which the straw is primarily cleaned before it enters the pulp boilers. The loss incurred by cleaning will depend upon the quality of the straw, but it should not exceed 5 per cent of the total weight operated on.

Digesting the Straw in Caustic Soda Lye.—The boilers usually employed for doing this are of the rotary type—either cylindrical or spherical. Very seldom are upright stationary boilers used. The reason for this seems to lie in the necessity of keeping the mass within the boiler in a continual state of motion, so that each particle of straw will be equally acted upon by the caustic lye. This cannot very well be attained in stationary boilers, even with the usual vom-

iting arrangement, because the chaff, when softened by the lye, sinks down into such a dense, solid mass as to interfere with the free circulation of the lye through it.

Of two rotary boilers mentioned, the spherical type offers certain advantages over the other. It occupies relatively less floor space, is more easily filled and emptied, and presents less radiating surface per unit of capacity. These boilers are usually provided with two man-holes and a blow-off cock, and are heated by steam injected through the trunnion. Motion is given to them by means of worm gearing fixed to the standards supporting the boiler.

The strength and volume of the caustic lye employed necessarily vary in different mills, according to the kind of straw used, and upon other conditions peculiar to the nature of the apparatus in use—*e. g.*: the steam arrangements of the mill. Both are slightly modified when barley straw is used alone, but as in actual practice the best results are obtained by mixing the different kinds of straw and keeping the mixture as nearly as possible constant, any rule laid down with respect to the proportion of caustic lye required is adhered to from day to day. The actual quantity of caustic soda, reckoned at 60 per cent alkali, also varies slightly with different kinds of straw, as well as on the temperature and speed with which the digesting operation is carried out. Where the temperature is high, and the time given for the boiling is long, the caustic is reduced to a minimum.

The following figures, representing the charge of a strawpulp boiler, are from actual practice:

Weight of straw (mixture of oat and wheat), lbs.	4,480
Gallons of caustic lye	1,610
Hours under steam pressure	4
Steam pressure above atmosphere (per sq. in.)	60
Maximum temperature (deg. F.)	307
Caustic lye	
Twaddell (deg.)	10½
Total weight in pounds	16,945
Percentage by volume of Na ₂ O	0.3249
Percentage by volume of 60 per cent alkali	0.5416
Total 60 per cent caustic soda in pounds	872
(Pounds of 60 per cent caustic alkali on 1 cwt. of straw=21.8)	

The operation of digestion is very simple. The pulp boiler is filled as full as possible with the cut and cleaned chaff, and the required column of caustic lye run in. The man-lid door is then put on and a small quantity of steam admitted while the boiler is made to revolve for fifteen minutes or so in order to soften the straw and cause it to subside to make room for more. When this is done, the lid is again removed, and the vacant space within the boiler filled up with more straw. In this way the charge of straw per boiler is increased from 15 to 20 per cent. When the boiler is thus filled and the man-lid fastened on, high pressure steam is injected into the charge through the trunnion, and the pressure gradually raised to the desired degree. The pressure varies in different mills, but as a rule it registers from 60 to 90 lbs. per square inch. This pressure is reached after about two hours' steaming, and is further maintained for four or four

and a half hours. In the meantime the boiler is kept continually revolving.

Washing, Breaking, Purifying and Bleaching the Straw.—After the digesting operation has been completed, the whole contents of the boiler are emptied into a tank placed beneath it, where the crude cellulose is washed with hot water. It is necessary to accomplish this work with the least possible quantity of water in order to avoid undue dilution of the waste lye. The most efficient method is that of the application of the principle of displacement as carried out in the lixiviating of ball soda in the Leblanc soda process. It is possible in manufacturing practice to remove 95 per cent of the soda associated with the boiled straw cellulose by this system of washing with a dilution of about one-third, that is to say, the pulp can be washed in the tanks with a quantity of water, represented by one-third of the volume of black lye associated with the pulp. The weakest washings from these vats are run to waste, as it does not pay to evaporate them even though the most refined system of evaporation be used for their concentration.

After the bulk of the black soda lye has been removed in the way described the crude cellulose is allowed to drain, and then conveyed to a breaking engine, in which it is broken up into pulp.

In this engine it is again washed to remove the last traces of soda, and a proportion of the intercellular matter surrounding the fibers, as well as any dirt, will pass away with the wash water. That part of the intercellular matter carried away is in a fine state of division, and if it be left in the pulp it is supposed to consume a large quantity of bleaching powder in the subsequent bleaching. As a matter of fact, however, if the straw be properly boiled in the first instance, the intercellular matter has little influence on the amount of bleach required to bleach unit-weight of crude product. It is possible to wash strawpulp in the breaking engine to such an extent as to seriously affect the yield of pulp, and therefore the bulk of the washing can be most advantageously done in tanks.

The report on sand-lime brick soon to be issued by the Geological Survey will show that sales of this product in 1915 were 170,643,000 brick, valued at \$1,135,104, which was an increase of 7,014,000 brick or 4 per cent in quantity and of \$76,592 or 7 per cent in value over 1914. Michigan was the leading state, reporting sand-lime brick marketed to the value of \$286,948 or over one-fourth of the quantity and value of the sand-lime brick sold in the United States. Minnesota was second and New York third. The sand-lime brick industry, after experiencing the ups and downs of a new industry, the report states, has become firmly established and has found "its place in the sun." Many operators are reported as enlarging the capacity of their plants in anticipation of increased business during 1916.

THE ACTION OF SALTS OF HYDROXY ACIDS UPON CHROME TANNING.*

By HENRY RICHARDSON PROCTER, D. Sc., and JOHN ARTHUR WILSON.

The theory of chrome tanning assumes that tanning will take place if the basicity and concentration of the chromium salt are properly regulated. But cases have arisen where skins would not tan in certain liquors, even when these liquors were rendered very basic. An investigation has revealed the interesting fact that the presence of salts of many, if not all, of the hydroxy-acids has a very marked influence upon the tanning power of chromium salts.

The first salt experimented upon was potassium sodium tartrate, ordinarily known as Rochelle salt. It was found that if much of this salt be added to a chrome liquor, the latter is rendered incapable of tanning. Such a liquor gives no precipitate when rendered slightly alkaline with sodium carbonate. Immediately after Rochelle salt has been added to a chrome liquor the latter may give a precipitate if rendered alkaline, but the precipitate will slowly redissolve. If the mixture of salt and chrome is allowed to stand for several hours before adding the soda, no precipitate is formed. It was noted further that an addition of Rochelle salt to a solution of chrome alum produces a change of color.

These preliminary experiments recall the fact that in qualitative analysis the presence of hydroxy-compounds prevents the precipitation of the metals as hydroxides. The metal ion enters, in the negative ion of such hydroxy-compounds, as tartrates and citrates. The action is reversible, but the complex ion formed is very highly ionized, and furnishes even less of the metal ion in solution than does the nearly insoluble metallic hydroxide. This accounts for the fact that Rochelle salt redissolves a precipitate of chromium hydroxide.

A chrome liquor was prepared from chrome alum by treating with sodium carbonate in the usual way. From this a series of eight solutions was prepared, varying in concentration of Rochelle salt as follows:

Solution No.	Grms. chrome oxide per liter.	Grms. Rochelle salt per liter.
1.....	13	50
2.....	13	25
3.....	13	10
4.....	13	5
5.....	13	2.5
6.....	13	1
7.....	13	0.5
8.....	13	..

Temperature 24° C.

Into each liquor was put a piece of calfskin which was in a practically neutral condition. The liquors were agitated occasionally, and at the end of 24 hours the skins were examined. That in No. 1 was of a bluish color, while that in No. 8 was rather a green, the others varying in shade from blue to green. The

*From the Journal of the Leather Chemists Association.

skin in No. 1 was unusually full and soft, this property becoming less and less marked in the others down to No. 8. But all the skins were nearly or quite tanned, excepting those in Nos. 1 and 2.

Upon adding 150 cc. per liter of N/1 sodium carbonate solution to each liquor, heavy precipitates formed in all but Nos. 1 and 2. In No. 2 there was a lighter precipitate, but in No. 1 there was none. Four hours later the skin in No. 2 was tanned, but that in No. 1 was still untanned. We added 300 cc. per liter of N/1 sodium carbonate, in two portions, to No. 1, and still no precipitate formed, although the liquor was now alkaline to phenolphthalein. Forty-eight hours later the skin was still not tanned.

To make certain that the action of the Rochelle salt was upon the chrome rather than upon the skin, we immersed a piece of skin in a solution of N/1 Rochelle salt for several hours, allowed it to drain, and then put it into a large volume of fresh chrome liquor. The volume of liquor was taken so large that, when the Rochelle salt diffused, its concentration would not be sufficient to prevent tanning. The skin tanned very well.

The piece of skin from No. 1, which had not tanned, was now washed, to free it from salt, and placed in a fresh chrome liquor. In a few hours it was completely tanned.

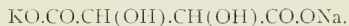
All of the above experiments were repeated with neutral sodium citrate, using equivalent concentrations. The results were apparently identical with those obtained with Rochelle salt. It was also found that the sodium salts of lactic, gallic, and salicylic acids prevent the precipitation of chromium in slightly alkaline solutions.

As to possible sources of these compounds in chrome liquors, it is conceivable that they might be formed in quantities sufficient to prevent tanning by reducing the bichromate with impure sugars or by reducing under improper conditions. Sugars themselves are hydroxy-compounds, and very probably yield an abundance of hydroxy-compounds of smaller molecular weights when the oxidation is very incomplete or is carried on at too low a temperature, and it is known that under certain conditions mucic and saccharic acids are formed by the oxidation of carbohydrates. An experiment was tried reducing bichromate at as low a temperature as possible with a commercial dextrine. The result was a liquor which did not at once give a precipitate upon rendering slightly alkaline and became turbid only on long standing. A piece of skin immersed in it tanned with difficulty, and only after adding an excess of sodium bicarbonate. In color and feel the leather resembled that from No. 2 in the experiments with Rochelle salt.

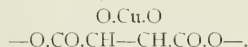
To deal with the very complex nature of the formation of hydroxy-compounds from the incomplete oxidation of the sugars is beyond the scope of our present research. We shall not even attempt an explanation of the exact reason why the chrome liquor in ques-

tion behaved as it did. It is sufficient for our purpose to state that, in order to insure the production of a satisfactory chrome liquor by reducing bichromate with sugars, it is necessary to use reasonably pure sugar, and conditions found to produce a satisfactory liquor should be closely adhered to.

Since sugars themselves are hydroxy-compounds, it might seem that an excess of sugar in a chrome liquor would prevent tanning. As a matter of fact, an excess of sugar, although it produces the fulness characteristic of the effect produced by Rochelle salt, does not prevent tanning, even when present to the extent of 20 per cent. An explanation of why sugars do not prevent tanning is offered by a consideration of the action of Rochelle salt in forming metallic complexes. Rochelle salt has the formula,



This salt ionizes not only into sodium, potassium and tartrate ions, but the tartranion ionizes slightly to a still further extent by giving off hydrogen ions from the hydroxyl groups. Since the sodium salt formed by replacing the hydrogen of the hydroxyl groups by sodium is readily ionizable, the addition of sodium hydroxide to a solution of Rochelle salt will result in the neutralization of the hydrogen ions, and a consequent increase in concentration of the tetravalent negative ion. But this negative ion forms with the heavy metal salts which are very slightly ionized. The most familiar example of this is found in Fehling's solution. When copper sulphate is added to an alkaline solution of Rochelle salt a slightly ionizable cupritartrate-ion is formed,



It is evident from the foregoing that, if the hydroxyl groups of a certain compound readily give off hydrogen ions, and if the resulting negative ion forms a very slightly ionizable salt with the heavy metals, no addition of alkali will be necessary to form the metallic complexes. But, if the hydroxyl groups do not ionize sufficiently readily an addition of alkali will be required to bring the concentration of the negative ion up to the point required to combine with the metal ion.

This is evidently the case with sugar. If the salt of a heavy metal is added to a solution of sugar, a considerable excess of alkali is required to form the complex. On the other hand, Rochelle salt forms the complex with chromium without addition of alkali.

The formation of the metallic complexes with hydrogen-compounds is discussed somewhat in detail because of its bearing upon points to be discussed presently.

It was originally intended that this research should consist only of a few simple experiments to determine possible reasons why certain chrome liquors refused to tan. But it soon became evident that the subject is rich in possibilities both for theoretical and practical work. Many ideas for the practical applica-

tion of the principles discussed presented themselves. Of these we shall mention the most promising, leaving it to those to whom any point appeals directly to carry on the research in greater detail.

Probably the most important property of Rochelle salt in this connection is its power to strip chrome leather of its chromium. This property was suspected from the fact that the salt will redissolve precipitates of chromium hydroxide. A piece of chrome leather was immersed in a normal solution of Rochelle salt over night. Upon subjecting to the boiling test, it was found to be no longer tanned. It was then washed and immersed in a fresh chrome liquor. It was again soon fully tanned, showing that chrome tanning is a reversible process.

Experiments were then tried to see how completely it was possible to strip the leather. A piece of air-dried chrome calf was immersed in a cold, normal solution of Rochelle salt and allowed to stand for two weeks. The liquor was colored a deep green. Upon being washed the skin resembled a bated calfskin, and was found to contain no appreciable amount of chrome. In this case the slow action was due to the low temperature of the liquor. A piece of chrome calf placed in such a liquor at 100° C. soon shrinks to a gummy mass.

There is a point which has long been a puzzle to many tanners. A hide is much easier to split after it has been chromed than in the raw state. But these tanners have not found nearly such a demand for chrome splits as for splits tanned with such materials as quebracho and mimosa bark. It might prove valuable to give the hides a light tannage with chrome, then split, and then strip the splits of their chrome by immersion in Rochelle salt solution. After washing they should be in a condition favorable for tanning with quebracho or mimosa bark.

Since hydroxy-compounds form complexes with other metals, including iron, Rochelle salt might conceivably be used for removing or preventing so-called salt stains. A stain produced by iron and sulphide was easily removed in this way. Treatment with Rochelle salt before liming might prove of advantage in some cases to prevent the formation of iron stains. The skins are easily washed free from the salt.

It is possible that a bath in Rochelle salt solution previous to tanning might be preferable to pickling for some kinds of leather. In the case of heavy leathers this possibly would result in a lighter, but more uniform, preliminary tannage. Such leather should be capable of taking up a much larger proportion of chromium upon being retanned in a fresh liquor, because of the even distribution of the chrome in the preliminary tannage.

While the presence of a large amount of hydroxy-compounds will prevent tanning, a small quantity does not, but does produce a fulness and softness in the leather not otherwise obtained. Many tanners have found that an excess of glucose in their liquors is

desirable. Probably small amounts of Rochelle salt would produce the desired effect. The point is at least worthy of consideration.

Another use of this salt lies in its power to strip chrome leather which has been case-hardened. If very basic chrome liquors are used in tanning there is danger of the interior of the skin absorbing acid while the chrome is being precipitated or fixed upon the surface. The surface becomes heavily tanned while the interior is still in a raw, acid condition. A very long time is required for such a condition to right itself, but the trouble could be overcome easily enough by stripping with Rochelle salt, washing, and retanning in a fresh liquor.

And finally, this stripping power of hydroxy-compounds can be applied to the conversion of chrome shavings and cuttings into glue stock. Pieces of air-dried chrome leather were stripped of their chrome and then converted into glue and gelatine in the usual manner. The importance of this fact needs no emphasis; it is obvious.

In all of the points discussed the theory of the formation of these complexes should be constantly borne in mind. It will then be evident that, in stripping, the solution must not contain any strong acid. The presence of acid would repress the ionization of the hydroxyl groups (in which hydron is liberated) to such an extent as to make the formation of these metallic complexes impossible. In fact, the addition of strong acid to one of these complexes will decompose it; the action being reversible. An alkaline solution is most favorable to the formation of these complexes, and where the presence of alkali will do no harm its presence will greatly accelerate the rate of action.

Since the property of Rochelle salt which has just been discussed is common, in a greater or lesser degree, to all hydroxy-compounds, the tanner has a wide choice in selecting substances most suitable for his purposes. Rochelle salt might prove too expensive to use freely as a stripping agent, but its use might be made practicable if the salt and chrome could readily be recovered. It is found that this can to a large extent be effected by the addition of sulphuric acid to neutralize the equivalent of soda and reconstitute the acid potassium salt, which is very little soluble and rapidly crystallizes out, so that it can be separated and used again with a suitable addition of soda, while the chrome can be precipitated from the mother-liquor as chromium hydroxide. Crude acid potassium tartrate ("tartar") dissolved with addition of soda would be the cheapest source of Rochelle salt. A mixture of equivalent quantities of lactic acid and sodium carbonate might serve his purposes just as well and would probably be a little cheaper. The practical applications of the principles discussed are problems for the tannery chemist, who, it is hoped, will find this work of value. It is also possible that uses may be found in other industries, as, for instance, in the stripping of chrome-mordanted wool.

CHILEAN NITRATE STATISTICS FOR FEBRUARY.

Both the production (5,292,841 Spanish quintals of 101.4 lbs.) and the exports (4,516,193 quintals) of Chilean nitrate for February according to a report of the U. S. Consul at Antofagasta, show decreases from the preceding month (production 5,641,671 quintals, exportation 6,247,402 quintals). The shorter month may easily account for the smaller production, but the decline in exports was due to a lack of cargo space. If a comparison be made with statistics for other Februarys the situation does not appear so unfavorable:

February—	Production. Quintals.	Exports. Quintals.
1912	4,210,559	3,721,280
1913	4,399,951	4,677,992
1914	4,747,026	4,640,584
1915	1,753,337	2,522,272
1916	5,292,841	4,516,193

The lack of vessels in which to ship nitrate is now beginning to be felt more seriously than before. It is reported that almost all the "oficinas" (reduction plants) in operation have large stocks of finished nitrate stored which they are not able to move for lack of ships. As payments for nitrate purchased under standard contract are made at time of shipment the stocks represent much capital rendered immobile. The lack of vessels and also the scarcity and high cost of coal are given as the reason for the closing of one oficina in March, and it is feared that others may be compelled to take the same course unless relief is soon afforded. The supply of fuel oil, used in many oficinas and being gradually substituted in many others for coal, has not been abundant, the supplying companies being barely able to fulfill their contracts.

Prices of nitrate are showing very little fluctuations at present, the price for ordinary 95 per cent ranging around 6s. 11d. (\$1.68 U. S. currency), for early delivery, while refined nitrate, 96 per cent-1 per cent, sells for around 7s. 3d. (\$1.76). To relieve, in some measure, the shortage of vessels the Chilean Government is permitting the available transports of its navy to carry nitrate for export. One of these, the *Maipo*, has already left this coast with a cargo of nitrate for the United States, and two others are being prepared for this service. The new oficina "Augusta Victoria," in the Aguas Blancas section of the Province of Antofagasta, began operations on February 15.

MARCH COTTON STATISTICS.

According to preliminary statistics prepared by the Bureau of the Census, Department of Commerce, the cotton consumed in the United States during March, 1916, amounted to 613,625 bales, and for the eight months ended March, 4,228,990 bales. The consumption for March, 1915, was 524,867 bales, and for the eight months ended March, 1915, 3,578,054 bales. The cotton on hand in consuming establishments on March

31, 1916, was 1,980,775 bales against 1,741,949 bales for the same period in 1915, and the amount in public storage and at compresses was 3,410,089 bales against 3,378,734 bales. Linters not included above were 80,905 bales consumed during March in 1916 and 33,234 bales in 1915. 158,143 bales on hand in consuming establishments on March 31, 1916, and 161,860 bales in 1915, and 209,992 bales in public storage and at compresses in 1916, and 100,387 bales in 1915. Linters consumed during eight months ended March 31 amounted to 635,015 bales in 1916 and 224,272 bales in 1915. Complete data as to the world's production of cotton for 1915 are not available. The estimated production for 1915 in the United States, India, Russia, and Egypt is 15,950,000 bales of 500 pounds net. The production in other countries in 1914, as compiled from the data available, was 2,990,000 bales.

The huge orders placed in this country for war materials have not only resulted in a great demand for chromium steels to be used directly for purposes of war but have led to the increased manufacture of special steels for cutting shells, rifle barrels, and other instruments of war, and are reflected in increased metal mining and greater consequent use of chromium steels for crushing machinery. Practically the only mineral used as a source of chromium is chromic iron ore, known as chromite. Chromite is largely imported, but importations have been much interrupted by the war, and as a result the production of chromic iron in the United States was last year greatly increased. Unfortunately for the consumers, nearly all of whom are east of the Mississippi, the production in the United States is wholly in California and to reach the greater market it has to be transported across the Rocky Mountains and Great Plains. At the end of the long haul, under ordinary conditions, it must compete with imported ore. However, there has been a sufficient decrease in freight rates to encourage production, and this with the irregularity of imports greatly encouraged the mining of the California ore in 1915. According to J. S. Diller, of the United States Geological Survey, whose report is now in press, the chromic iron ore marketed in 1915 amounted to 3,281 long tons, valued at \$36,744. In 1914 only 591 long tons, valued at \$8,715, was sold.

The wheat crop of 1915 was an exceptionally good one, the total world production being 4,000,000,000 bushels, an increase of 800,000,000 bushels over the production of 1914, according to preliminary figures given in the bulletin of the International Institute of Agriculture in Rome. More than 90 per cent of the 1915 wheat crop, or 3,675,000,000 bushels, was produced in the Northern Hemisphere, while 325,000,000 bushels came from the Southern Hemisphere.

THE USE OF NICKEL HYDROXIDE IN TANNIN ESTIMATION.*

By PURAN SINGH and T. P. GHOSE, B.Sc.,
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As shown in a paper on this subject by one of us (*J. S. C. I.*, 1911, 30, pp. 936-937), freshly precipitated nickel hydroxide serves as an excellent substitute for hide powder in the estimation of tannin. Situated as we are in India, our supplies of standard hide powder at times run short, and a reliable substitute for hide powder is a great desideratum. With this object in view, we have continued our experiments on the use of nickel hydroxide as a substitute.

Dr. H. H. Mann, of the Poona Agricultural College, was kind enough to compare the nickel hydroxide method with the copper acetate method, which he has been using for years in tannin estimation, and with the hide powder method, with the results shown in Table I.

TABLE I.

	Babul pods (Pods of <i>Acacia auriculata, arabica</i>).	Tarwar (<i>Cassia auriculata</i> , whole plant).
	Tannin pct.	Tannin pct.
Nickel hydroxide paste method.....	26.3	0.7
Hide powder method.....	23.7	0.84
Copper acetate method.....	26.6	0.60

A practical difficulty, however, confronted us in the preparation of pure nickel hydroxide free from sulphate. In the form of freshly precipitated paste, we found it extremely difficult to wash it free from sulphate except in very small quantities. The word "paste" carried no definite idea of the percentage content of nickel hydroxide contained in it. For these reasons, we had eventually to abandon the use of paste and to use the fine powder of nickel hydroxide instead. For the purpose, we obtained Kahlbaum's extra pure nickel hydroxide, which, to our great surprise, contained traces of sulphate. After repeated washing with hot water and finally with water containing traces of tannic acid, we got it free from sulphate and in a fairly granular condition. This nickel hydroxide has been used in the experiments described in this paper.

TABLE II.

Serial No.	Description.	Quantity contained in 500 cc. grms.	Quantity absorbed by nickel hydroxide powder, grms.	Quantity absorbed by chromed hide powder, grms.
1	Tannic acid.....	4.56	4.26	4.41
2	Gallic acid.....	4.52	3.92	3.12
3	Glucose.....	4.76	2.06	2.36
4	Cane sugar.....	4.94	2.79	2.39
5	Tannic acid and gallic acid.....	2.28	3.90	3.00
6	Tannic acid and glucose.....	2.28	2.55	2.26
7	Tannic acid and cane sugar.....	2.28	2.43	2.48

It has already been shown that nickel hydroxide forms definite chemical salts with tannic acid (*J. S. C. I.*, 1914, 33, pp. 172-173, this Jour., 1914, pp.

186-8). It also forms an insoluble salt with gallic acid. The solutions of tannic acid, gallic acid, glucose, and cane-sugar of known strength were treated, with chromed hide powder and nickel hydroxide under similar conditions, with the results shown in Table II.

These tests gave sufficiently encouraging results to make comparative estimations with a number of tanning materials, the results of which are shown in Table III.

TABLE III.

Description of material.	Tannin by Mois- nickel hy- ture. droxide. hide pct. pct. powder.	
	pct.	pct.
Mangrove bark.....	12.02	33.95
Mangrove extract.....	14.33	73.13
Sal (<i>Shorea robusta</i>) bark.....	10.19	19.59
Sal extract.....	16.09	62.57
<i>Cassia auriculata</i> bark.....	9.89	23.42
<i>Cassia auriculata</i> bark.....		23.23
Myrobalans, pulp.....	14.98	58.95
Myrobalans, pulp, another sample.....	9.59	57.20
Myrobalan extract made at Dehra Dun	11.19	52.16
Gambier (3.56 per cent ash).....	9.83	60.40
Commercial Katha from Dabura Bazar*	5.02	17.63
<i>Terminalia tomentosa</i> bark.....	7.81	10.41
Babul pods with seeds.....	10.64	10.70
Babul (<i>Acacia arabica</i>) bark.....	9.41	13.31
Pulp of fruits of <i>Zizyphus xylopyra</i>	10.50	31.31
<i>Cassia fistula</i> bark.....	7.91	14.09
<i>Rhus cotinus</i> leaves.....		13.57
<i>Rhus cotinus</i> leaves, a poorer sample.....	10.73	5.49
<i>Rhus cotinus</i> leaves, another sample.....	11.26	5.27
<i>Rhus cotinus</i> leaves, another autumn sample from young tree.....	9.76	16.54
<i>Rhus cotinus</i> leaves, from old tree.....	10.30	25.28

From these results we conclude that instead of nickel hydroxide paste, as originally proposed, the nickel hydroxide should be used in the form of powder. All other precautions as to extraction and the concentration of tan liquor remain the same; instead of hide powder 20 grams of nickel hydroxide free from water should be added for detannization. Only in the case of Babul pods it was seen that the nickel tannate formed was in such a minute state of division that it would not settle, and the filtrates obtained were somewhat turbid. This was overcome by mixing the filtrates with well dried kaolin and passing once more through fresh filters.

We are using this method of tannin estimation in this laboratory, and we consider that it is as reliable as the hide powder method, perhaps preferable to it, considering that nickel hydroxide is, unlike hide powder, a standard substance, and that this method can be used in all cases where organic and mineral acids likely to dissolve nickel hydroxide are not present.

DISCUSSION.

Mr. J. T. Wood asked Professor Procter what advantage, if any, nickel hydroxide had over sprouted alumina; the latter was a definite compound, and seemed to absorb tannin and reject gallic acid; that was what was wanted.

Professor Procter said that however excellent nickel hydroxide might be as an absorbent material, it was hardly worth discussing, at least for commer-

*From Journal Society Chemical Industry.

*A sample heavily adulterated with clay (65.65% ash).

cial purposes, as the method could only be empirical and the hide powder method under present conditions had firmly established itself as an empirical commercial method, and also had the advantage, perhaps not very real but appealing to the tanner, that it attempted to be an actual tanning process on a small scale. Nickel hydroxide was not by any means the only material which could be used successfully in a similar way. In 1904 Professor H. Wislicenus (see *J. S. C. I.*, 1904, 765) prepared aluminum hydroxide by treating the metal with a trace of mercuric chloride, with which he obtained results probably as satisfactory as those with nickel hydroxide, but which for the reasons cited above never came into use. Probably also other hydroxides might be substituted in the same way. Nickel hydroxide seemed to be inferior to hide powder as regards distinguishing gallic acid from tannin, though neither was particularly satisfactory in that respect. Some of the results with particular tannins and with mixtures of tannin and gallic acid also appeared to be anomalous. But if nickel hydroxide were more easily obtained in remote districts than hide powder, there seemed to be no reason why the method should not be used as a preliminary one in forming a judgment for forestry purposes. A method was quoted, but without reference, for the determination of tannins with copper which also appeared, at least in the cases noted, to give satisfactory results. It had long been known that copper methods with certain tannins were capable of considerable concordance and accuracy, but a large class of tannins gave precipitates which were soluble in ammoniacal copper solutions, and for which therefore these could not be used. It was possible, however, that some copper salt of a suitably weak acid, or copper sulphate mixed with a neutral salt of such an acid, might be used direct to precipitate tannins, and if a method of that sort could be found which would give rapid, if even only approximate results, it would be of great value in the practical control of the tanning process, for which a rapid method was much wanted, even if it were quite unsuitable for the commercial analysis of extracts. On theoretical grounds he was extremely doubtful whether most of the tannins were capable really of forming definite salts at all; certainly most of the compounds should rather be regarded as colloidal precipitates than as true salts in the ionic sense.

Mr. Wilkie referred to the paper by D. B. Dott, in which the use of copper salts was advocated.

Mr. Wood said that the only criticism Mr. Dott had made was that two chemists did not get identical results. The results appeared to show satisfactory concordance in the case of sumac, although the extraction appeared to have been at fault. In a paper which he (Mr. Wood) had read at Brussels some years ago, he showed that it was impossible to obtain identical results because the colloidal precipitate varied.

Professor Procter said that an ingenious method had been suggested at one of the meetings of the Leather Chemists' Association, in which the tannin solution was put in an aluminum basin and an alternating electric current passed through the basin, producing alumina; it appeared to give very satisfactory results as compared with other methods, including the hide powder method. Sumac was an extremely difficult material to extract satisfactorily.

EXPERIMENTS WITH BRINES IN SEARCH FOR POTASH.

Several deep holes have been sunk in the deserts of Nevada and one is being drilled in the panhandle of Texas under the supervision of the United States Geological Survey in the search for potash. The Survey is also making some laboratory experiments designed to aid in discovering a cheap process of separating potassium salts from natural brines.

Since the importations of potash salts from Germany were stopped, the urgent need of a domestic supply has greatly increased and the price of high-grade potash has advanced from \$39 to about \$500 a ton. Efforts to find commercially workable deposits in this country have been eagerly and diligently made, both by private capitalists and public agencies. The Survey has endeavored both to find deposits of soluble potash salts and to discover practicable methods of extracting potash from rocks that carry relatively large proportions of potassium. Every clue that might yield valuable results has been followed up in a country-wide investigation, extending from New York to California.

In the laboratory experiments special attention has been given to the evaporation of brines rich in potassium. The results of some of the earlier work were published late in 1915 as Professional Paper 95-E. More recent experiments have been made with the natural brine from Searles Lake, Cal., which contains the equivalent of nearly 12 per cent of potassium chloride in the solid salts. The results are given in a recent survey publication, "Evaporation of brine from Searles Lake, Cal.," issued as Professional Paper 98-A. This report shows the changes in the composition of the solution resulting from the evaporation of the brine, the composition of the crystals deposited from the hot solution during evaporation, and the composition of the crystals deposited when the solution was cooled. A copy of the report may be obtained free of charge by addressing the United States Geological Survey, Washington, D. C.

The data recorded indicate that carefully controlled fractional evaporation and crystallization, possibly combined with other treatment, promise much as a means of obtaining potassium from brines similar to that of Searles Lake. Further study of the behavior of the constituents of the brine under varying conditions may be made.

THE REMOVAL OF THE NATURAL IMPURITIES OF COTTON CLOTH BY THE ACTION OF BACTERIA.*

By B. S. LEVINE.

The ordinary process of bleaching cotton cloth consists of: (1) a treatment for the removal of certain of the natural impurities which may be present; and (2) a bleaching proper, which decolorizes any impurities left after the preliminary treatment. The natural impurities of the cotton fibers have been studied by several investigators with no apparent relation to the processes of purification of cotton cloth, and by the writer of this paper in connection with a study of the bleaching process. According to the results obtained, the impurities of cotton fibers can be classified for practical purposes as follows: *water-soluble, alcohol-soluble, mineral, ether-soluble, impurities and nitrogenous coloring matters.*

Not all of the above named impurities, as has been shown by Hebden,¹ are responsible for the yellowing of clothing during the steam test or during storage. According to his opinion, the presence of the alcohol-soluble and of the nitrogenous substances only is responsible for a bleach being imperfect. From a study of the ether-soluble, alcohol-soluble and nitrogenous constituents of the growing cotton fibers,² we were able to corroborate the conclusion of Hebden with regard to the significance of the nitrogenous constituents of the cotton fibers in bleaching, but our unpublished results of a study of cloth in different stages of the bleaching process and of the nature of the alcohol-soluble and ether-soluble impurities of cotton showed that the first, contrary to the opinion of Hebden, have no connection with the yellowing of cloth, whereas the presence of the latter, to which Hebden had ascribed no significance; bears in the yellowing of bleached cloth a share fully equal to that of the nitrogenous substances.

In connection with the determination of a convenient index of purity of cotton cloth, the question has come up whether the present processes of bleaching do not effect any structural differences in the cellulose molecule, thus making it possible to suppose that the quality of a bleach might be due to structural rearrangements. Accordingly, samples of cotton cloth in different stages of bleaching processes obtained from several bleacheries were analyzed for the percentages of carbon, hydrogen, and of oxygen, and tested for their reactivity to certain chemical reagents. From the results obtained, the conclusion was drawn that no structural differences were brought about in the fiber molecule, and that a bleach may be considered to be "good," when all or most of the nitrogenous and ether-soluble substances have been removed from the fibers. Thus, it may be said that the impurities which

the bleaching process is supposed to remove or decolorize are the non-cellulose constituents of the cotton fibers, and that they are apparently in no chemical union with the molecules of the fibers. As they are of an organic nature, it seems possible that they might be rendered soluble by the action of certain enzymes of animal or vegetable origin, and that the action of any of these biological agencies upon cotton cloth would result in an efficient and perhaps cheaper method of purification of fabrics.

For some time the writer has been engaged in a study of the principles underlying the action of different enzyme preparations, of moulds, and of bacteria upon the impurities of cotton. The present paper deals with the study of the bacterial treatment of cotton cloth for the purpose of removing its impurities preliminary to bleaching.

PRELIMINARY INVESTIGATION.

The analysis of cloth in different stages of the bleaching process and a knowledge of the nature of the non-cellulose constituents of the cotton fiber make it clear, as summarily indicated in the introduction, that if bacteria are to be used for the purification of the cloth preliminary to bleaching, only those which can bring about all or some of the following transformations can be employed:

I—Those which render soluble or otherwise removable the coagulated non-soluble nitrogen-containing constituents of the fibers.

II—Those which render soluble or otherwise removable the alkali-resistant waxes and the fixed fats of the fibers which are represented by the ether extracts.

III—Those which render easily removable the substances which are related to the pectoses.

Most of the soil bacteria and also some of the bacteria which causes certain plant diseases fulfill some or all of the above conditions. The ammonifying and denitrifying bacteria of the soil, as is well known at present, decompose a large amount of organic matter in the form of fat, waxes, oils, pectins, gums, and celluloses in order that they may get the necessary energy for the metabolism of the living cell. The bacteria which causes the root-rots of certain plants produce strong pectin decomposing enzymes. The cellulose-destroying bacteria, as was pointed out by Herbert³ in 1892, do not attack the cellulose molecule

¹Ann. Agron., 18 (1892), 536-550.
proper before the pectins, gums, tannins, and other non-cellulose substances have been utilized by them. Thus, the number of bacterial species possessing one or more of the properties required for our purpose is very large, and the question which arose in connection with our problem was not "Can the fibers be purified by bacteria," but, "Which species of bacteria shall we employ for the solution of our problem?"

To answer the above question a number of bacterial species were secured, some of which were soil bacteria, some intestinal bacteria, and some plant pathogens. These were obtained from the collection at the Mu-

*From The Journal of Industrial and Engineering Chemistry.
¹Hebden, Journal of Industrial and Engineering Chemistry, 6 (1914), 714.

²Levine, Sci. N. S., XL1, 1058 (1915), 543-545.

seum of Natural History in New York, from the Vermont Agricultural Experiment Station, and some were isolated by us. In all cases the identity of the species was established by determining their morphological and physiological characteristics. The selection of those best suited to our purpose was made in the following way: Flasks of standard broth and of synthetic medium (to be described later) were inoculated with the different strains and incubated at 37.5° C. from 10 to 14 days. Cotton yarn, which was thoroughly "wetted out" and sterilized in the autoclave, was introduced into the flasks and they were again incubated for periods not exceeding 10 days. The yarn was then taken out, properly labeled, washed in hot water, and boiled for 5 minutes in a 1 per cent solution of caustic soda. It was then subjected to the

which depends upon the amount and diffusibility of the enzyme produced. Hence, from the amount of substrate transformed, the enzymic strength of the bacteria may be determined by plating the bacteria out on agar containing a known per cent of the substrate and incubating for a few days. The enzyme excreted by the organism usually diffuses equally in all directions, and the circular zones around the colonies may be made visible by treating the plates with suitable reagents. The diameter of the circle can be measured and compared with that of zones produced by other organisms on the same substrate and their relative efficiency may thus be ascertained. The zone formed by a bacterial colony has been called the "enzymic zone" and its diameter expressed in millimeters or fractions thereof.

TABLE III.—TESTS OF CLOTH SAMPLES AFTER THREE MONTHS' INCUBATION.

No.	Culture.	Starch Test.	Starch Transformation Indicated.	Softening of Cloth.	Strength of Cloth.	Condition of "Motes."	Bleached Samples (a) Color.	Motes.
C ₁	<i>B. amylolyticus</i>	Faint violet	Partial removal of amyloextrins	Considerable	Unimpaired	Strongly discolored	White	None
C ₂	<i>B. bibulus</i>	Very faint green	Change or solution of dextrins	Decided (b)	Weakened (c)	Mostly gone	Very white	None
C ₃	<i>B. fini</i>	Negative	Changed to sugars or achroedextrins	Decided (d)	Impaired (c)	Mostly gone	Whitest of all	None
C ₄	<i>B. carotovorus</i>	Very light green	Removal of dextrins	Considerable	Unimpaired	Mostly gone	Very white	None
C ₅	<i>B. subtilis</i>	Violet (greenish)	Further change in amyloextrins	Some	Unimpaired	Swollen and discolored	White	None

(a) See text for method of bleaching.

(b) Pinkish tint. (c) Signs of disintegration where the cloth was not wholly submerged and came in contact with the air.

(d) Pink tint lighter than C₂.

TABLE I.—TESTS OF CLOTH SAMPLES AFTER ONE MONTH'S INCUBATION.

No.	Culture.	Starch Test	Transformation to a Dextrin	Softening of Cloth.	Condition of "Motes."
A ₁	<i>B. amylolyticus</i>	Violet-blue	Probable	Slight	Merely swollen
A ₂	<i>B. bibulus</i>	Violet	Probable	Less than A ₁	Swollen and slightly discolored
A ₃	<i>B. fini</i>	Greenish	Decided	Considerable	Swollen and slightly discolored
A ₄	<i>B. carotovorus</i>	Greenish	Decided	Considerable	Swollen and slightly discolored
A ₅	<i>B. subtilis</i>	Greenish violet	Less than above	Moderate	Swollen and discolored

TABLE II.—TESTS OF CLOTH SAMPLES AFTER TWO MONTHS' INCUBATION.

No.	Culture.	Starch Test.	Change beyond 1 Mo.	Condition.	Softening of Cloth.	Condition of "Motes."
B ₁	<i>B. amylolyticus</i>	Violet	Not marked	More than A ₁	Same as A ₁	
B ₂	<i>B. bibulus</i>	Greenish	Marked	Much more than A ₂	Almost completely gone	
B ₃	<i>B. fini</i>	Light green	Decided	Much	Barely colored and partly gone	
B ₄	<i>B. carotovorus</i>	Light green	Decided	Moderate	Swollen and slightly discolored	
B ₅	<i>B. subtilis</i>	Greenish violet	Not marked	Slight	Swollen and slightly discolored	

bleach and sour as in the ordinary bleaching process, washed, dried, and steam-tested. The cultures which gave the best results were selected for further experiment. They were the following:

<i>Bacillus amylolyticus</i>	n. s.
<i>Bacterium fini</i>	n. s.
<i>Bacillus bibulus</i>	n. s.
<i>Bacillus carotovorus</i>	n. s.
<i>Bacillus subtilis</i> (Ehrenberg)	Coln

All these bacterial species produce enzymes by means of which they perform the transformation of such substances as sugars, starches, gums, pectins, celluloses, and various proteins into substances, the molecules of which are much smaller than and possess chemical properties differing from those of the original substances, so that they can be easily distinguished from them. Thus the starches are broken down to dextrins and to dextrose, the pectins are changed to pectic acid, the celluloses to carbon dioxide, methane, various organic acids, and water. The proteins are broken down to carbon dioxide, water, ammonia, nitric and nitrous oxides, free nitrogen, and perhaps some other compounds. These bacterial enzymes diffuse in the surrounding media to an extent

To further test the suitability of the strains previously selected, the bacteria were grown on cellulose-agar plates, starch-agar plates, pectin-agar plates, and their enzymic zones measured. The starch and the cellulose-agar were prepared as follows:

Cellulose-Agar.	Starch-Agar.	Pectin-Agar.	Amounts.
Cellulose Solution	Starch Solution	Pectin Solution	500 cc.
Nutrient Solution	Nutrient Solution	Nutrient Solution	500 cc.
Agar	Agar	Agar	10 g.

The cellulose and the starch solutions were made up according to the directions given in Bulletin 266, United States Department of Agriculture, Bureau of Plant Industry, page 28. The pectin solution was prepared from the water-soluble substances of cotton in the following way: Unspun non-absorbent cotton was percolated with water for 24 hours, the cotton pressed out and the solution filtered to clearness; it was then evaporated to dryness on a steam bath, and 10 g. of the dried extract were dissolved in 500 cc. of water. The nutrient solution consisted of 1 g. each of dibasic potassium phosphate and magnesium sulphate, 2 g. each of sodium chloride, ammonium sulphate and calcium hydrate, and 1,000 cc. of water.

The bacteria were plated out on each of the media described and incubated at 37.5° C. in a chamber saturated with moisture so as to prevent drying of the plates. After 10 to 14 days' incubation, the enzymic zones were measured. The results were as follows:

	ENZYMIC ZONES.		
	Starch.	Cellulose.	Pectin.
<i>B. bibulus</i>	1.0 to 2.0 mm.	0.1 to 0.3 mm.	1.0 to 1.5 mm.
<i>B. fimi</i>	2.0 to 3.0 mm.	0.5 to 1.0 mm.	0.5 to 1.0 mm.
<i>B. amylolyticus</i> ..	0.5 to 1.0 mm.	0.5 to 1.0 mm.	?
<i>B. carotovorus</i> ..	1.5 to 2.0 mm.	?	1.5 to 2.5 mm.
<i>B. subtilis</i>	?	0.2 to 0.5 mm.	0.7 to 2.0 mm.

It may be seen from an examination of this table that the transforming strength of the enzymes produced by the bacterial strains selected was great in all cases, and that their suitability to our work, as determined by the previously described flask-incubation method, was confirmed.

ACTION OF BACTERIA UPON THE IMPURITIES OF COTTON CLOTH.

The bacterial strains selected as previously described were employed further in the study of the action of their enzymes upon the impurities of cotton cloth. Five hundred cc. of the nutrient solution described above and 50 g. of coarse cotton cloth containing about 5 per cent by weight of starch as a "sizing" material were put in each of 15 flasks and sterilized in the autoclave for 30 min. Sets of 3 flasks were then inoculated with the liquid cultures of the bacteria employed and incubated at 37.5° C. Control flasks with the nutrient solution and cloth were sterilized as described above and incubated without having been inoculated. One sample from each of the cultures was then taken out 1 mo., 2 mo., and 3 mo. after inoculation. The samples were thoroughly washed in boiling water to remove all the soluble products of the bacterial metabolism and the adhering chemical reagents of the medium, and the samples taken from the flasks incubated for 1 and 2 mo. were tested for starch; the samples taken from the flasks incubated for 3 mos. were tested for starch, nitrogen, and ether- and alcohol-soluble substances. The strength of the cloth, its softness, and the disappearance of the "motes" were also noted. The results appear in Tables I, II and III.

Samples from all the 3-mo. incubations were bleached for 4½ hours in a solution of freshly prepared calcium hypochlorite of 2° Tw. They were then thoroughly washed in cold water and put into a solution of sodium bisulphite (4° Tw.) for another 4½-hour period. After this, the cloth was thoroughly washed, dried, ironed, and compared as to whiteness, with the results noted in the last two columns of Table III.

The bleached samples were then subjected to the steam test under a pressure of 10 lbs. per sq. in. for 45 minutes. None of the samples were yellowed by such treatment, and we assumed, therefore, that all the substances which cause yellowing of the bleached cloth during steaming or during storage were removed.

In order to determine whether the removed substances were the same as determined by the analysis of cloth in the different stages of the bleaching process, the bleached samples from the bacterial treatments were analyzed for the determination of the percentages of the ether-soluble, alcohol-soluble, and nitrogen-containing substances which were left in or on the fibers after the "chemick" and the "sour." The results are given in Table IV.

The cloth incubated in the control flasks after the 3-mo. incubation showed no starch transformation, very slight reduction in the percentage of the ether-soluble and nitrogen-containing substances, and no change in the percentage of the alcohol-soluble substances.

In all the bacterial treatments, the nitrogen-containing substances were removed from the cloth completely, the ether-soluble substances were removed more efficiently than they were after the chemical process of bleaching, the alcohol-soluble substances remained unchanged, except in the case of the cloth subjected to the action of cultures of *B. carotovorus* and of *B. subtilis*.

The weakening of the cloth in the samples subjected to the action of cultures of *B. bibulus* and of *B. fimi* may have been due to the action of the oxygen of the air on those parts of the cloth saturated with the calcium hydroxide of the media which were not completely submerged. It is possible also that during the long period of incubation to which the cloth was subjected, the bacteria may have acted upon it to such an extent that a slight general disintegration was caused.

But as the reactivity of the cloth remained apparently unchanged, we feel safe in concluding that a more thorough investigation of the action of some of the bacteria upon the impurities of cotton cloth would determine the conditions under which the bacteria would remove the nitrogenous and ether-soluble substances of the fibers without impairing the body of the fabric.

THEORETICAL CONSIDERATIONS.

The question may be asked in connection with the disappearance of the insoluble nitrogen-containing substances of the cotton fibers: "How have they been removed to such an extent by the action of bacteria?" The transformation of nitrogenous substances which is usual in the case of decomposition of organic matter in the soil, suggests a way in which the answer might be given. To determine whether the case in our experiment was similar to that of the above mentioned condition in the soil, we tested several samples of media, taken out at various times of incubation, for the presence of ammonia. The quantity of cloth and the small percentage of the nitrogenous substances in it rendered our attempts fruitless. We were about to give up further investigation along that line, when we found in some of the flasks a very slight, white precipitate. On testing, it proved to be calcium carbonate, and it at once occurred to us that in the

presence of calcium hydroxide the decomposition of the nitrogen-containing substances may be accompanied by the formation of calcium carbonate, free nitrogen or ammonia, and water.

The nitrogenous coloring substances of cotton in the American and the Egyptian varieties were studied by Dr. Schunk,⁴ and according to his analysis the formula for the substances found in the American variety would be $C_{10}H_{12}O_4N$, and that of the substances found in the Egyptian variety $C_{23}H_{30}O_9N_3$. In the presence of calcium hydroxide the reactions brought about during the decomposition of the first by means of oxidation may be represented by the following equations:

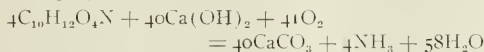
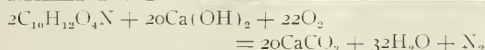
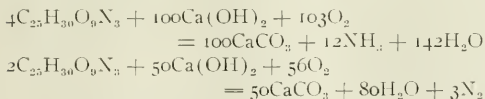


TABLE IV.—TESTS SHOWING REMOVAL OF IMPURITIES FROM CLOTH SAMPLES BY INCUBATION FOR THREE MONTHS AND SUBSEQUENT BLEACHING.

	Grams Orig-	Grams Incu-	Nitrogen (or Protein),		Per Cent	Total
			After	Removed by		
			"Sour"	Incuba- tion "Sour"		
<i>B. amylolyticus</i>	0.156	0.0032	None	75.8	24.2	100.0
<i>B. bibulus</i>	0.156	Trace	None	100.0	...	100.0
<i>B. fimi</i>	0.156	0.0038	None	97.9	2.1	100.0
<i>B. carotovorus</i>	0.156	0.0025	None	84.4	15.6	100.0
<i>B. subtilis</i>	0.156	0.012	None	92.9	7.1	100.0
Ether Extract.						
<i>B. amylolyticus</i>	0.392	0.059	0.015	78.8	9.3	88.1
<i>B. bibulus</i>	0.392	0.0716	0.0446	78.6	9.3	87.9
<i>B. fimi</i>	0.392	0.117	0.041	85.0	11.2	95.2
<i>B. carotovorus</i>	0.392	0.075	0.039	80.9	9.1	90.0
<i>B. subtilis</i>	0.392	0.125	0.079	68.1	11.2	79.3
Alcohol Extract.						
<i>B. amylolyticus</i>	0.5107	0.5107	0.4569	0.0	3.2	3.2
<i>B. bibulus</i>	0.5107	0.5107	0.472	0.0	3.0	3.0
<i>B. fimi</i>	0.5107	0.5107	0.4098	0.0	2.5	2.5
<i>B. carotovorus</i>	0.5107	0.323	0.306	35.9	5.2	41.1
<i>B. subtilis</i>	0.5107	0.465	0.457	8.9	2.5	11.4



and for the oxidation of the latter in the presence of calcium hydroxide the reactions may be represented as follows:



Free ammonia and free nitrogen are thus formed which could not be detected by us on account of their small amounts. As there was no precipitate found in some of the flasks, it may be supposed that mere liquefaction of the protein substances took place which rendered possible their complete removal after the strong oxidation during the "chemick" which had most probably converted the peptones and amino acids formed into nitrates and nitrites.

The reactions just given are of the nature of oxidations and result in liberation of energy. It therefore seems probable that the nitrogenous substances of the cotton fibers form some sources of energy to the bacteria. The pectins, gums, and waxes, no doubt,

are used up by them first, the nitrogen-containing substances next, and, as the medium used in our experiments was devoid of carbohydrates, the cellulose finally was drawn upon by the bacteria as a source of energy. This probably would not be the case in the practical application of bacteria to the treatment of cotton cloth before bleaching, as the period of incubation would have to be reduced to a minimum. The weakening of the cloth would be eliminated entirely, and a cheaper, safer, and more convenient process for the purification of cotton cloth preliminary to its bleaching would thus be obtained.

Since the conclusion of the above described preliminary experimental investigations, studies have been carried on with a view to applying bacteria to practical purification of various cellulose fibers. By using different combinations of bacterial species, different media, different reactions of the media to start with, and different temperatures during the period of incubation, the latter was reduced to 72, 48, 36, and in some cases even to 24 hours, all depending upon the nature of the fibers used.

A number of tests on a large scale were also performed for the purification of paper-making stock in connection with one of the eastern paper making factories, and for the purification of cotton yarn and cotton cloth in connection with some of the Rhode Island bleacheries. In all cases the results obtained were very encouraging.

SUMMARY.

I. Of all the natural impurities of cotton cloth only the nitrogen-containing and the ether-soluble substances, when insufficiently removed from the cloth previously to the "chemick," cause yellowing of bleached cloth in the steam test or during storage.

II. The nitrogenous substances of the fibers were broken down by bacteria so that they were completely removed from the cloth. This transformation in the presence of the calcium hydroxide has probably resulted in some cases in the formation of either free ammonia or nitrogen, calcium carbonate, and water, and in some in the reduction of the nitrogenous substances to peptones and amino acids which are easily oxidized to nitrates and nitrites.

III. The ether-soluble substances of the cloth were removed in our experiments by bacterial treatment more efficiently than is the case in the ordinary bleaching process.

IV. The alcohol-soluble substances were very little attacked by the bacteria, probably because of the formation of a calcium salt in the presence of the calcium hydroxide of the media.

V. None of the bacteria experimented with have transformed the starch of the cloth any further than to dextrins.

VI. Bacteria may be profitably employed as a substitute for the present method of purifying cloth preliminary to its bleaching.

The present paper records a part of the work done

⁴Memoirs, Manchester Literary and Philosophical Society, Vol. IV, 3rd Series.

by the author along similar lines for Mr. J. C. Hebden of Providence, R. I., in connection with and under the auspices of the Biological Laboratory of Brown University. The author wishes to express his gratitude to the instructing staff of the Brown University Biological Laboratory and to Mr. Hebden for their general and generous assistance in the work and for permission to publish the results.

HYDROGEN FOR MILITARY PURPOSES.*

By EDWARD D. ARDERY.†

One thousand cubic feet of hydrogen will lift about 70 pounds; the same volume of coal gas about 35 pounds. According to the purity of the hydrogen, its lifting capacity varies. One process gives gas with a lifting power of about 1.19 kilograms per cubic meter, another 1.183 kg., another from 1.175 to 1.195 kg.

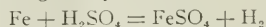
The ascensional force of gases depends upon their specific gravity, temperature, and the barometric pressure of the atmosphere. The ascensional force of any gas equals the weight of air minus the weight of an equal volume of the gas. Hydrogen has twice the ascensional force of pure coal gas, and is universally used for military balloons. Hydrogen permits the employment of smaller balloons, which facilitates transportation and rapid filling, besides affording a smaller target at which the enemy may shoot.

About ten years ago there was constructed a welding torch using oxygen and hydrogen gases, by means of which iron, steel, and other metals could be perfectly welded. About six years ago the blowpipe process of cutting metals was discovered. The construction of oxy-hydrogen blowpipes requires the hydrogen outlets to be capable of supplying four volumes to one of oxygen, for the preheating flames. A torch constructed on this principle cuts almost as well as the oxy-acetylene flame, but is not so efficient in starting the operation of cutting, for the reason that it is necessary, on a flat surface, to make some small projection which the oxy-hydrogen flame can seize, in order to start the heating of the plate. The water vapor produced causes considerable oxidation of the metal when it is brought to the melting point. By using four volumes of hydrogen to one of oxygen this defect is in a measure overcome; but oxy-hydrogen can never be as efficient for welding as oxy-acetylene, for the reason that by the use of excess hydrogen the oxidation by water vapor is only abated and not eliminated. No matter how great the excess hydrogen, the effects of the water vapor still exist. In cutting metals, however, the defects arising in welding are not so marked; and the oxy-hydrogen flame can be used with success where the supply of hydrogen is abundant and inexpensive, as is the case where an electrolytic oxygen plant is used. One cubic foot of

hydrogen produces 350 B. T. U., and the temperature produced at the tip of the torch, at four volumes to one, is approximately 4,200° F. (2,315° C.) as compared with 6,300° F. (3,482° C.) produced by oxy-acetylene. Hydrogen for welding is probably best suited only for thin sheet iron, and is perhaps no more efficient than illuminating gas.

Both of these processes might on occasion prove of considerable value in military operations. The welding might be utilized in making light repairs to machinery, gun carriages, wagons, etc. The cutting would no doubt prove useful in cutting debris and wreckage, destroying wire entanglements, cutting bridge members, railroad track, etc.

For military purposes, however, hydrogen would find its greatest use in inflating balloons, either captive or free. To generate the hydrogen gas readily and in sufficient quantities, recourse has been had to various processes. Probably the first method used consisted in employing iron filings and dilute sulphuric acid. In this process the iron filings should be free from rust, and the gas evolved should be cleaned by passing through a water seal and lime purifier. The reaction is given by the formula:



Similarly, zinc may be used instead of iron. The gas from zinc and sulphuric acid is purer than when iron is used. 100 lbs. of sulphuric acid and about 140 lbs. of zinc give 1,000 cubic feet of hydrogen. A balloon with a capacity of 16,000 cu. ft. would thus require about two tons of these materials.

In the Russo-Japanese war the Russians used a process based on the action of aluminum on sodium hydroxide. This method presupposes an ample water supply, and has the drawback that it requires 5½ kg. of materials for every cubic meter of hydrogen produced. The apparatus consisted of sheet metal containers, each of which was partly filled with sodium hydroxide. The aluminum chips were held in a gauze drum, a portion of which rested in the liquid. From the producer, the gas passed through the washer and from there to the balloon.

In the Morocco campaign, the Spanish government used a producer developed by Schneckert & Co. Instead of using aluminum, silicon was employed. At temperatures of from 80° to 90° C. the action of this element on sodium hydroxide is energetic. The temperature need not be attained by the use of fuel if the natural development of heat during the solution of the caustic soda in water, while forming the solution, is utilized. Preparations for starting the generator consist merely in pulverized caustic soda being poured during stirring into a vessel containing water, thus getting a solution of 90° C. in temperature. By turning on a cock this solution is admitted to the generator vessel, and silicon is added. During the formation of the gas, which lasts about 50 minutes, water is again run into the dissolving vessel, and caustic soda in pieces added, which quickly dissolves with the aid of

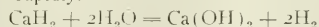
*Paper read before the New York Section of the American Electrochemical Society, in joint session with the New York Sections of the American Chemical Society and the Society of Chemical Industry, on Feb. 11, 1916.

†Captain, Corps of Engineers, United States Army.

the hot hydrogen touching the sides of the solution vessel. This enables a new cycle to be commenced with only a few minutes interruption, at the end of every generating process. When the formation of gas is finished, the generator contains a solution of water-glass, a non-injurious liquid, which can be let out without special precaution. The temperature reached does not exceed 110°C . The apparatus is made of iron, and not being subject to chemical or mechanical destruction, it is of practically unlimited durability.

The French have used ferro-silicon instead of silicon. The producing apparatus is called "Silicol." Another method originated by the French is called the "Hydrogenit" process. This is particularly adapted for use where an abundance of water is not available. "Hydrogenit" is a mixture of finely powdered ferro-silicon and sodium-calcium oxide. It is a gray, sandy substance, which, even in a closed receptacle, burns with a large production of hydrogen. The mixture is ignited by means of a match or a small amount of ignition powder. It comes in sheet metal containers, and is said to keep indefinitely at normal temperatures. These containers are placed bodily in the producer and fired. The producer is surrounded by a water jacket, the contents of which are eventually converted into steam. Towards the end of the process, the steam is shot into the chamber to accelerate the action. The gas is washed in water and then dried by passing through screens of sawdust and coke.

Calcium hydride, a substance known commercially as "Hydrolith" (CaH_2), if dropped into water, evolves hydrogen rapidly.



The objection to it is its excessive cost. A sodium base may be used instead of calcium, but great care is necessary to prevent ignition of the hydrogen by the heat of the chemical reaction. "Hydrone" is another substance that requires only the addition of water to produce hydrogen.

A German corporation has perfected the old method of producing hydrogen by passing steam over red-hot iron filings. The steam is dissociated, the oxygen combining with the hot iron to form black oxide of iron (Fe_3O_4), leaving hydrogen free. The iron is then regenerated by blowing over the oxide hot water-gas containing a large percentage of carbon monoxide. The black oxide gives up oxygen and is reduced to spongy iron. The process may be made continuous by using two ovens.

In manufacturing nitrogen and oxygen from the air, low temperatures are employed, but these temperatures are not low enough to effect the separation of hydrogen from water gas. Water gas consists of about 50 per cent of hydrogen, carbon monoxide, and some nitrogen. It also contains a comparatively small percentage of CO_2 , which is first eliminated by passing the gas over caustic potash. The gas thus purified is compressed to about 30 atmospheres, and cooled to a temperature in the neighborhood of the boiling point of oxygen, say 200°C . The liquefiable con-

stituents are the CO and N , whose critical temperatures are, respectively, -136° and -146°C . When allowed to escape from an open valve at the temperature of its surroundings, hydrogen, however, does not cool, but rises in temperature. Thus the regenerative method applied in the liquefaction of air is not applicable for cooling down water gas. Liquid air is therefore resorted to, the requisite degree of cold being obtained by allowing it to evaporate. In spite of the efforts to eliminate CO_2 and water vapor, traces of these bodies pass into the separating apparatus and are deposited there in solid form, ultimately obstructing it after the lapse of a certain time. By having duplicate plants, one can be worked while the other is brought back into working shape by heating it and blowing gas through it.

The Signal Corps of the U. S. Army has made experiments with a view to obtaining hydrogen by refrigerating illuminating gas.

A method invented by two Dutch engineers is used both in Germany and in Russia. This process uses the gas produced by the fractional distillation of crude oil and tar. The gas is passed through a layer of hot coke, whereby the hydrocarbons break up with ultimate liberation of hydrogen. The product delivered contains from 2 to 3 per cent of CO , which is removed by subsequently treating with hot sodium oxide. Oil-gas, crude oil, petroleum by-products, tar, benzol, or benzine may be employed in the same process. Charcoal can be used instead of coke. The oil, which has been previously heated, is introduced as a spray at the top of the producer. The coke is brought to a white heat by a hot-air blast. As the oil eventually cools the coke, production is intermittent.

Hydrogen is also a by-product in the electrochemical manufacture of caustic soda and sodium from sodium chloride.

Hydrogen may be obtained from the electrolysis of water by using lead electrodes and a dilute sulphuric acid electrolyte, or iron electrodes and a 10 to 20 per cent solution of potash. If a solution of KOH is used, electrolysis causes the oxygen to combine with the anode, while hydrogen is liberated at the cathode. At intervals the decomposed water has to be renewed, while the potash remains in solution, and there is practically no loss. The electromotive force required is about 3 volts per cell.

Our army installed a plant at Fort Omaha, Nebraska, for generating hydrogen by the electrolysis of water. Thirty cells were used. One thousand five hundred amperes of direct current were passed through the cells in series. The voltage varied from 85 to 120, depending on the internal resistance of the cells.

In the original electrolytic plants each cell formed an independent unit, and had with the others a positive and a negative connection, and, furthermore, a separate pipe line for hydrogen and for oxygen. The filter press system of Surth came into use about eight years ago. The Surth system is used extensively by

Germany for military purposes. The apparatus consists of a number of cells forming at once the electrodes and the storage tank for the electrolyte. The cells are composed of a special metal which is attacked by neither the oxygen, alkali, nor electric current. These cells are pressed together and form a hermetically closed tank. The electrodes are connected in series. The separation of the gases formed is effected by means of special asbestos tissue. This tissue is placed between the anode and cathode, and separates them positively from each other. At the same time, it permits an easy passage for the electrolyte, and insulates both electrodes from each other. In this manner they form a bipolar electrode; that is, they are positive at one side and negative at the other. Each electrode has in its upper part two connecting canals. One of them has the connection to the positive side and the other has a connection to the negative side, so that all oxygen goes in one canal and all hydrogen in the other. The whole apparatus is filled with electrolytic solution. In the interior of the apparatus there is no accumulation of gas. The electric current goes through the whole apparatus and develops on the surface of each electrode the corresponding gas. For an apparatus of 180 to 200 cells there is provided only one draw-off for hydrogen and one for oxygen. There is only one intake for water. Electrodes that have been working four years have shown no sign of wear.

Hydrogen gas from oil-gas is about 98.4 per cent pure, with a specific gravity (aid = 1) of 0.087 to 0.092. From water gas the hydrogen is 97 to 97½ per cent pure; but if this be passed over soda-lime the resulting gas contains as its only impurity 0.6 to 0.8 per cent of nitrogen. A percentage of 97 to 97½ hydrogen corresponds to a density of 0.094, while when the percentage of hydrogen is raised to 99.2 or 99.4, the density falls to 0.077. Schuckert's metallic silicon process gives hydrogen at least 99 per cent pure, and free of poisonous or injurious admixtures. The Saurth electrolytic process gives gas 99.8 per cent pure.

Stationary plants, usually providing for generation on a large scale, must necessarily be designed along lines more economical than for portable plants. Stationary plants would find use at aeronautic establishments, army centers, and at points where gas is generated to be compressed into cylinders for shipment. Stationary plants may have capacities for generating 300 cubic meters and upwards per hour. The smaller sizes of apparatus would probably weigh about 4,000 kg. net, or 5,500 kg. packed for ocean shipment; the larger sizes, 9,500 kg. net, and 12,000 kg. gross, no piece weighing over 2,000 kg. The electrolytic plant installed at Fort Omaha in 1908 had a capacity of 3,000 cu. ft. (85 cu. m.) per hour. To follow an army's movements, portable plants are necessary. These should permit of being mounted on cars or wagons. Some plants can be set up on shipboard, some on three or fewer railroad cars, and others on

wagons. The capacity of portable plants varies from 9 cu. ft. (0.25 cu. m.) per hour to (50,500 cu. ft.) 1,600 cubic meters per hour.

The weights of portable plants depend, of course, on the capacity and type of plant. Schuckert's generator cars weigh about 2,000 kg. each, and the scrubber cars about 1,700 to 2,100 kg.

In comparing the relative cost of portable plants and stationary plants distributing by means of steel tubes, consideration should be given to the cost of the tubes, their weight to be transported, and the cost of compressing the gas.

For transporting in campaign, hydrogen may be absorbed by some chemical substance dissolving it or giving with it a combination capable of restoring it easily and rapidly whenever wished. Hydrolith and hydrone are in this class. Or, the gas may be compressed in steel tubes. Some French tubes are about 4 meters long, 270 millimeters interior diameter, and 6 mm. thick. Other dimensions are used at sea and in the colonies. In order to avoid explosions, tubes have been tried with diameters of 45 to 400 mm.

Our service employs cylinders about 7 feet (2 m.) long, and 5½ inches (14 cm.) in diameter; and also some about 4 feet (1.2 m.) long and 8½ inches (22 cm.) in diameter. They are made of cold drawn seamless steel tubing.

The weight of steel cylinders is less than the weight of the iron and sulphuric acid necessary to produce an equal volume of hydrogen. The weight of our tubes does not exceed 100 lbs. (45 kg.) each. In the French service, each wagon carrying tubes weighs 3,000 kg. for about every 15 kg. of gas transported, or about 200 times the weight of the hydrogen. They contain 200 liters of gas at 133 kg. pressure: equivalent to about 25 cu. m. at atmospheric pressure. The German flasks hold about 36 liters of gas at a pressure of 130 atmospheres, which corresponds to about 5 cu. m. of balloon space. Some American flasks contain 100 and 200 cu. ft. (3 to 6 cu. m.). In some cases compression is done at from 150 to 200 atmospheres (2,200 to 2,940 lbs. per sq. in.). Pressures as low as 700 lbs. (47 at.) have been used, to prevent explosion. Tanks used in welding or cutting are charged to about 100 or 150 lbs. (7 to 10 at.). In our service the tubes are tested with hydraulic pressure up to about 5,000 lbs. (340 at.) and are charged to about ½ of the pressure used in testing. All our cylinders have a safety outlet blowing at 3,500 lbs. (238 at.). Our 7 feet by 5½ inches (2 m. by 14 cm.) tubes have a capacity of about one cubic foot (28 liters) and are ordinarily charged to 120 atmospheres.

For German conditions it has apparently been found that the best method of bringing gas to the balloons is not to bring the producer to the front, but to send forward the hydrogen in steel flasks. The flasks are transported in caissons, 20 to each vehicle, and it is so arranged that six caissons can be coupled together when the balloon is to be filled. The French have

some wagons that carry six tubes. The transportation of hydrogen in steel tubes is quite an old practice. The English have used tubes since 1882; the Italians, since 1887.

The Germans fill a 600 cubic meter balloon from 120 flasks in about 20 minutes. Using oil gas for producing hydrogen requires one to two hours to fire up. According to the size of the plant being used, Schuckert's metallic silicon process allows of a full production of hydrogen to be reached in from 10 to 45 minutes from the time the command is given. Other processes require different periods of time before gas becomes available for inflation; so the compressed gas in flasks has a considerable advantage as far as the time factor is concerned. Their two principal objections are the danger of explosion and the dead weight to be carried.

A pipe line for carrying hydrogen is in successful operation in Germany. The line is $4\frac{1}{2}$ kilometers long, and can supply 1,000 cubic meters of gas daily. This requires as pressure of 1,000 millimeters (water column). It discharges into a storage tank. The joints of the pipe are welded autogenously for most of the length, unions being installed at long intervals.

The cost of production varies, of course, with the size of the plant, market and labor conditions, and the process used. Some of the *alleged* costs per cubic meter (35 cu. ft.) of hydrogen gas, according to the process used, are: Ferro-silicon 20 cents, hydrogenit 32 cents, hydrolith 100 cents, steam and hot iron filings 3 cents, distillation of crude oil and tar $3\frac{1}{2}$ cents, water gas 25 cents, old method of iron and sulphuric acid 25 cents, calcium hydride 175 cents, silicon and caustic soda 210 cents. By electrolysis, 1,500 amperes produce 23 cu. ft. (0.66 cu. m.) of hydrogen and $11\frac{1}{2}$ cu. ft. (0.33 cu. m.) of oxygen per cell per hour.

As I have shown above, the lifting power of a balloon depends on the gas used to inflate it and on the volume of the balloon. The temperature and barometric pressure of the atmosphere affect the density of the gas, and hence its ascensional force. A captive spherical balloon cannot be used when the wind is greater than twenty miles an hour.

The usual fixed balloon has a capacity of 600 cubic meters. The dirigible balloons have capacities up to possibly 60,000 cubic meters. It is stated the German dirigible that descended in France in 1913 had a volume of 20,000 cubic meters and a lifting capacity of 20 tons. The normal working internal pressure is understood to be 2 oz. per square inch (0.0085 atmosphere). Cotton, silk, goldbeater's skin, and various rubberized fabrics have been used as balloon envelopes. Silk is objectionable on account of its cost, and on account of its accumulating static electrical charges. Great Britain has used goldbeater's skin. Rubberized fabrics oxidize and crack. The envelope should be strong, elastic, impermeable to gas, water repellant, and of light weight. Chlorine attacks balloon envelopes.

Hydrogen is so light that in case of leaks, even low down in the envelope, the gas rises; but if mixed with air in a balloonet it becomes heavier, descends, and may be exploded by a spark from the engine.

Without going into the theory of ballooning, I might add that unless the balloon envelope is elastic, a rise in altitude of 125 ft. (38 m.), or a rise in temperature of the gas of $2\frac{1}{2}^{\circ}$ F. (1.4° C.) necessitates the loss of gas. Goldbeater's skin allows a rise to 2,000 ft. without loss of gas. As fuel is used up or explosives dropped, the tendency of the lightened balloon is to rise, thus probably causing a loss of gas. In dirigible, it must be borne in mind that ordinarily there is sufficient lifting capacity only when the motors are running. If they stop, the vessel must descend or jettison some ballast.

A trip of about $8\frac{1}{2}$ hours from a base in Germany to the English coast would mean the use of about $1\frac{1}{2}$ tons of fuel. If $1\frac{1}{2}$ tons of explosives are carried, a state of static equilibrium will have been attained by the time the coast is reached.

The hitherto too rapidly fluctuating buoyancy of the airship may now be controlled through the use of the graduated motor exhaust, which is evenly distributed by ducts throughout the entire air-jacket between the outer and inner hulls, and the same system enables the passing of hot and cold currents through the air-jacket at the will of the operator. These alternate hot and cool currents expand or contract the gas, producing rapid ascent or descent. This device has assured a static gas, which maintains the airship for long periods at normal buoyancy.

If the air-jacket contains a charge of nitrogen gas, this not only insulates the hydrogen from atmospheric effects, but acts as a sure preventive of fire risk. Both of these methods have proved easy of accomplishment. The exhaust of the motor has been freely discharged into a balloon containing hydrogen, without setting it afire. Experiments with the nitrogen jacket are said to have demonstrated the complete success of this method, which explains the story about the Germans using non-inflammable gas.

STRONTIUM IN 1915.

The manufacturers of red fire and of beet sugar are said to have shown considerable interest in domestic strontium deposits during the last year. If sugar holds its present price the beet-sugar makers might perhaps profitably substitute the strontia method for the one they now use, but the substitution will require considerable time and its economy must depend on several economic factors which are unknown to the United States Geological Survey, by which the statistics of the industry are compiled. The returns received by the Survey do not show that any strontium-bearing ores of domestic origin were sold in 1915 or that any American deposits were exploited.

The deposits in northwestern Ohio and southeastern

Michigan seem to be the best available for early exploitation. Celestite, a strontium mineral, is reported to occur in workable quantities in certain limestone quarries near Toledo, Ohio, though it is not now recovered. The mineral is found in broken and open beds of dolomite, or magnesian limestone. The installation of expensive machinery for its recovery is hardly warranted, but the larger pieces of celestite could be easily hand-sorted from limestone on picking belts, or possibly on the ground, and would probably find a market.

Large deposits of celestite occur in Arizona and California, but they are far from markets and of low grade as compared with commercial ores now used. Plants for making commercial strontium compounds may eventually be built at places where both these sources could be drawn upon, but the development of these deposits must wait on the decision of the sugar refiners to adopt the strontia process.

Most of the commercial ores used in making strontium salts are of high grade, containing at least 95 per cent strontium sulphate. English celestite is at present largely used on the eastern seaboard and is laid down at the works at about \$12 a ton, so the owners of deposits of strontium ores must not hope for large profits on their crude material.

The principal commercial strontium salts are strontium hydroxide, used in the beet-sugar industry, and strontium nitrate, used in pyrotechnics, in which, however, strontium chloride is also used. Small quantities of certain organic and inorganic salts, such as acetate, lactate, bromide, iodide, arsenite, and phosphate, are used in medicine.

Strontium nitrate was formerly used in making some types of smokeless powder, but the powder companies, it is said, now use the salts of strontium only for making illuminating or signal shells, in which the value of the strontium lies in the brilliant red color it imparts to the flame produced by explosion.

The imports of strontium oxide, protoxide of strontium, and of strontianite, or mineral carbonate of strontia, in 1914, as reported by the Department of Commerce, were valued at \$1,016, and in 1915 at \$6,411. The imports of celestite (strontium sulphate) used by domestic manufacturers of strontium salts are not recorded, as this mineral is classified with other chemicals not specially provided for. Strontium salts are imported free of duty.

FUEL BRIQUETTING INDUSTRY IN 1915.

Over a million dollars worth of briquets were made out of waste coal dust in 1915, the exact production being 221,537 short tons, valued at \$1,035,710. This was the largest output in the United States for any year with the exception of 1914. The manufacture of this type of fuel is, however, still in its infancy, and according to C. E. Leshar, of the United States Geological Survey, a good many years will probably elapse before the briquet industry assumes very large proportions. The work of briquetting this low-grade

material and converting it into fuel suitable for higher uses is, however, practicable conservation and as such deserves far more attention than it now receives in this country. European countries, more thrifty in their use of coal, have developed the briquetting industry to large proportions. Most of the mechanical difficulties of manufacture have been solved in this country and the future growth of the industry now depends upon the development of markets for the product. The producing plants are, however, so widely distributed and the total production is so small compared with that of other kinds of fuel that the conditions affecting the market for the output of each plant are more or less local and peculiar. In general, in the East, briquets compete with anthracite as domestic fuel, and nearly all the output of the eastern plants is manufactured from anthracite culm. The people of the eastern cities, accustomed to the incomparable anthracite, have not taken very kindly to these briquets, probably largely because of the volume of tarry smoke given off by nearly all kinds of briquets when they are first ignited, and perhaps partly because it has not been possible to offer them at a price enough lower than that of anthracite to induce their extended use. Being made from the cheaper sizes of anthracite, the briquets contain a greater amount of ash than the domestic sizes, and although this ash does not clinker in the furnace it reduces the heat value of the fuel.

There were 15 briquetting plants in operation in the United States in 1915, one less than in 1914. One new plant in California reported an output in 1915, and 2 plants, 1 in New Jersey, and 1 in New York, ceased operations. The greatest increase in output was made on the Pacific coast, the central states recording little change and the eastern states a large decline in output.

Manufacture Research by Department of Commerce.

A bill has been introduced in the House of Representatives by Representative Mann, of Illinois, which authorizes the Department of Commerce to make original investigation and research concerning forms and processes of manufacture. Mr. Mann's bill is H. R. 7134 and has been referred to the Committee on Interstate and Foreign Commerce. The measure is as follows:

Be it enacted, etc., that the Secretary of Commerce is hereby authorized through the Bureau of Standards, or any other bureau now under the Department of Commerce, or which may be hereafter created in said department, to make original investigation and research concerning forms and processes of manufacture and needs and methods for improvement in manufacture, both generally and specially; but no process or device which may be discovered or invented by any person while employed in or by said department in accordance with the provisions of this act shall be patented for the use or special benefit of any person, but the same shall be open for the general use of all. For the purposes herein indicated the Secretary of Commerce may employ such experts, special agents, clerical assistants and other help as may be authorized from time to time by law.

The CHEMICAL ENGINEER

PUBLISHED MONTHLY by the MYRON C. CLARK
PUBLISHING CO.

608 S. Dearborn Street, Chicago

*Entered as Second Class Matter, Aug. 19, 1907, at the Post Office
at Chicago, Illinois, under Act of March 3, 1879.*

Subscription—United States, Cuba and Mexico. \$2.00
Extra postage to Canada 25c a year; to foreign countries 50c a year.
Remittances may be made by check, draft or money order in favor of
THE CHEMICAL ENGINEER

All communications should be sent to THE CHEMICAL ENGINEER, 608
S. Dearborn Street, Chicago, Ill.

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NOTES AND COMMENTS.

American Substitute for English Whiting.

Manufacturers who use whiting, an essential constituent for certain ceramic glazes and bodies, generally have imported this material from England. However, a sample of calcium carbonate, recently submitted as a by-product by a firm in Baltimore, has been found by the United States Bureau of Standards to be an excellent substitute for this English whiting. It gave very desirable and satisfactory results in the trials which were made of it. Two very refractory plastic clays have been encountered in the routine testing of clays submitted by various parties, both of which are promising for the manufacture of glass pots and crucibles. One is from Cecil County, Md., and the other from near Nashville, Tenn. Thermo-couple tubes previously manufactured by the Bureau of Standards have all been made by molding through a die, but the bureau is now able to produce some very satisfactory tubes by casting in plaster molds.

Preparing Standard Screen Scale.

Plans have been made for a conference of representatives of various committees of engineering and industrial societies at which it is proposed to discuss

the preparation of a standard scale of sieves for the use of all industries employing fineness tests. Two proposed scales have been tentatively agreed upon—one based on integral metric units and one on the customary units—and the conference has been arranged with a view to their final adoption. Upon the preparation of specifications for each of the sieves the United States Bureau of Standards will be prepared to extend the list of sieves which it tests and certifies to include this series of standards.

Mechanical and Magnetic Properties of Steel.

A review of the work done in correlating the magnetic and mechanical properties of steel has been published by the United States Bureau of Standards in its Scientific Paper No. 272. The magnetic method tests the whole amount of material and not merely some surface phenomenon. It does not destroy the test piece, but leaves it unaltered. Thus it is found to be possible to apply a magnetic test to the identical material that is to enter into a given structure. Copies of the publication, the title of which is "Correlation of the Mechanical and Magnetic Properties of Steel," will be sent free upon request to the Bureau of Standards, Washington, D. C. The International Association for Testing Materials has designated the subject covered in this book as one of the important problems of today, and has assigned its investigation to a special committee.

Saponin Barred From Food Products.

The addition of saponin to food mixtures which are sold for use in place of white of eggs is regarded by the Bureau of Chemistry of the Department of Agriculture as constituting adulteration within the meaning of the Food and Drugs Act. In "Service and Regulatory Announcements No. 17" it is stated that the practice is usually adopted for the purpose of concealing inferiority and that therefore it comes within the definition of adulteration in the Food and Drugs Act. Saponin is used extensively in so-called substitutes for white of egg for the purpose of producing foam and thus giving the articles a fictitious appearance of body and therefore of food value. Saponin is a substance that when dissolved in water foams like soap. It is extracted from plants known as soapbark and soaproot, and a few other plants, by boiling them in water. Its name is derived from the Latin word *sapo*, which means soap. When saponin is added to the so-called substitutes for white of eggs it produces a foam similar in appearance to the foam produced by genuine white of egg.

Adhesion Tests for Fabrics in Rubber Industry.

The United States Bureau of Standards has installed in its rubber-testing laboratory a newly designed autographic machine for testing the "friction" or adhesion between the different plies of canvas used in rubber hose, rubber belting, automobile tires, etc. This machine, by means of a diagram that is made

automatically during the test, shows the exact value of the adhesion between adjacent layers of fabric at all points. The machine was designed and built at the Bureau of Standards. The bureau is experimenting with several rubber compounds that have been made into eyeshades for use in connection with the range finders on battleships. Some of these shades have been molded in the bureau's experimental laboratory and will be tested in service to ascertain the compound best suited for such use. An important recent test was in connection with fire hose purchased for use in the District of Columbia. Samples representing 28,000 feet of fire hose were tested both physically and chemically to determine if the specifications had been complied with.

Wider Range in Study of Expansion of Materials.

By using a bath of pentane the range of temperatures for determining the expansion of materials has been extended by the United States Bureau of Standards to -150°C ., so that the bureau can now carry such measurements in an oil bath from -150° to $+330^{\circ}\text{C}$. Rods of very pure tungsten, of cold-drawn 36% nickel steel (invar) and of porcelain, have been measured for variation of coefficient within this range recently. The bureau is also preparing to investigate a large series of copper alloys and brasses both parallel to and perpendicular to the direction of rolling. In heat testing the bureau has made an accurate determination of the melting point of gold for an industrial research laboratory; calibrated two standard pyrometer lamps recently; compared a copper-constantan thermocouple and a platinum resistance thermometer at temperatures extending as low as liquid-air temperatures; determined the melting point of two samples of zinc; and made a life test of base metal thermocouples.

Experiments with Silver Voltameter.

The results of a careful series of measurements to determine the amount of impurity contained in deposits of silver made in the "silver voltameter" have just been published by the United States Bureau of Standards in its Scientific Paper No. 271. The silver voltameter is the international standard for the precise measurement of electric current. This work points to a correction of the value of the "Faraday," which is an important constant in physical chemistry and certain branches of theoretical physics. Copies of the publication, entitled "Inclusions in the Silver Voltameter Deposits," will be sent free to persons interested upon request to the Bureau of Standards, Washington, D. C.

Putting Paper Industry on Scientific Basis.

The attempt to place the paper industry of the United States upon a more scientific basis in its manufacturing processes received material support at the first annual meeting of the comparatively new Tech-

nical Association of the American Pulp and Paper Industry. The paper expert of the United States Bureau of Standards was among the large number who attended the sessions, and the Bureau's co-operation with the work of the association was tendered. Methods of test and standard specifications for raw materials and finished products were discussed, interesting papers were read, and plans were made to evolve from the organization a clearing house for technical problems arising in the paper industry. During the month of February the Bureau of Standards made tests on 144 samples of paper for the United States Public Printer, 115 for the various executive departments and independent establishments, and 26 for persons and firms that had applied to the Government. This yielded a total of 285 samples for the month. There have been various other instances in which the services of the bureau were extended in matters relating to this industry. Assistance was given the Smithsonian Institution in obtaining samples of the highest grade papers. The problem of increasing the opacity of book papers without increasing the weight or decreasing the strength was taken up. The photographing of colored papers was studied. A representative of the largest clay company in the United States visited the bureau to discuss the utilization of domestic clays for paper making.

Increased Use of Electric Furnaces.

John M. Savage, U. S. Consul at Sheffield, England, reports under date of March 1 that until the past year the use of electric furnaces in Sheffield was limited and not more than ten were in operation in all the steel works located here. During the calendar year 1915, however, at least fifteen additional electric furnaces were installed in various works or are in process of installation, and a large number of manufacturers have the erection of such furnaces under consideration. As a result of the increased production owing to the introduction of these furnaces a largely increased output of alloy steel for the construction of automobiles, aeroplanes, and small castings has resulted, and at present there is a large demand for these types of steel. Numerous experiments have and are being made for the melting of "high speed" steel in electric furnaces, but Sheffield manufacturers are not yet convinced that this process produces as good an article as that obtained by the crucible process that has been in use for so many years. The principal drawback found here to the electric process for the latter steels is the undue size of the melts, and it is claimed much better results are obtained in teeming the smaller quantities handled by the crucible process.

Fish-oil extractors are also sharing the general prosperity which the war has brought with it. Their goods are, it is to be particularly noted, being shipped to America in an ever-increasing quantity.

The Chemical Engineer

PUBLISHED MONTHLY

at 608 S. Dearborn Street, Chicago, Illinois

Vol. XXIII.

CHICAGO, MAY, 1916.

No. 5.

AMERICAN DYESTUFF PRODUCTION IN 1914 AND 1916.

The preliminary figures on the manufacture of dyestuffs in 1914, as summarized by the Bureau of the Census, reveal the extent to which this country depended upon foreign sources for the element of color, as far as it is contributed by materials of an organic nature. These constitute almost entirely the dyes used in the textile branches, as well as in the manufacture of paper and varnish, the dyeing of feathers and straw, etc.

During the calendar year 1914 the production of synthetic dyestuffs in the United States amounted to about 3,300 short tons, valued at about \$3,000,000. The importations of coal-tar dyestuffs from Europe for the fiscal year 1914 were 25,700 short tons, valued at \$9,102,000. The domestic production was, however, confined largely to the assembling into finished dyestuffs of semi-manufactured materials. The only genuinely American contribution consisted in about 900 tons of aniline, made from benzol of domestic origin, the manufacture of which was started in 1910. Six factories were devoted to this branch, and 400 operatives were employed.

The advent of the war involved an almost complete cessation in the shipment of the coal-tar "intermediates" employed in our dyestuff plants, as far as they were of German origin. Since March, 1915, no artificial dyestuffs have been received from Germany, which formerly contributed 86 per cent of our foreign supply.

All American industries dependent upon the use of artificial colors—and they are scores in number—were threatened by paralysis or discoloration.

Under untoward conditions American chemists and American capital have grappled with a serious problem and sought to relieve temporary distress, while laying the foundations for a comprehensive, self-contained American coal-tar chemical industry which should free us from dependence upon trans-Atlantic sources.

During the past year and a half a large amount of constructive work has been done. It has meant the creation of the industry from the bottom up, the multiplication of sources of coal-tar "crudes," the organization of the manufacture of the many "interme-

diates," and the construction of new units for the production of finished colors.

The recovery of coal-tar "crudes" from the by-products of coke plants has now been so perfected that the output is more than sufficient to cover the needs of a national color industry. Two years ago the annual output of these crudes was estimated as follows: Benzol, 9,600 short tons; toluol, 3,200 tons; naphthaline, 1,500 tons; and phenol, 75 tons. Today the estimated annual output is: Benzol, 90,000 tons; toluol, 22,440 tons; naphthaline, 12,500 tons; phenol (chiefly synthetic), 10,000 tons.

About thirty-three companies, many of which are, however, small, are now occupied with the manufacture of coal-tar intermediates. The leading product is aniline, of which the output for 1916 will exceed 15,000 tons. Over 3,000 tons of other intermediates are currently produced by the same companies. Large additional amounts are made in the works of the companies directly engaged in manufacturing colors and making their own intermediates.

The number of these latter has expanded from six in 1914 to sixteen in 1916. Many of these sixteen are small concerns engaged in experiment work and in laying the foundation for future development. The current output represents an annual production of 15,000 tons of finished dyes. Of this amount about 3,000 tons is aniline used directly in dyeing aniline black upon fabrics, replacing temporarily an equivalent amount of sulphur black.

To a notable extent this sudden expansion in the American output of synthetic colors is due to the multiplication, on a vast scale, of the facilities for the production of direct blacks and sulphur blacks, thus meeting the most pressing needs of the textile interests, and effecting the largest possible manufacture of coloring material at a minimum expenditure of time and effort. There has, however, been a regular production of other colors, especially of blues, and steps are being taken to rapidly increase the extent and variety of the output in this field.

American dye producers have not reached and can not be expected to reach for probably some years the efficiency of the German manufacturers. The American consumer can not at present expect to obtain from our manufacturers the variety of colors developed in the German industry, and perfection of qual-

ity will come only after time has served to develop the industry of this country. The German industry is the result of years of research, technical training, and specialization.

Less spectacular, but still of marked interest, has been the evolution in the use of natural dyestuffs by American manufacturers. The Bureau of the Census reports a domestic output of such dyes in 1914 valued at \$1,866,000. The chief constituent was logwood extract, amounting to 14,500 short tons, and valued at \$1,312,000. This represents an increase for this dyestuff of 32 per cent over the production of 1909. Other natural dyestuffs (quercitron, fustic, cutch, archil, etc.) increased in value from \$144,000 in 1914 to \$544,000 in 1915, or 285 per cent.

It is evident that during the past few years there was a notably enlarged appreciation of the real value of natural dyestuffs on the part of American textile manufacturers. Colorists were gradually recognizing that the marvelous ease of application, attendant upon the use of synthetic dyes in most cases, had led to a neglect of natural colors, not justified by their unquestioned worth, under suitable conditions. Processes were perfected which broadened the field of application and heightened the degree of fastness attainable upon the use of individual vegetable dyes.

Under the pinch of famine conditions this trend has been swiftly accentuated. American extract works were fortunately in a position to enlarge their output rapidly, and were hampered only by difficulty in securing raw material from the West Indies and elsewhere as quickly as wanted.

As a result, it may be claimed that the natural dyes have materially aided in lessening the acuteness of the shortage in colors, and that they have been restored to a position which they should legitimately occupy in the well-balanced, systematic tinctorial methods. There has been an increased recognition of the technical value of our indigenous quercitron and the utilization of the handsome yellow obtained from our osage orange in place of imported fustic has become an accomplished fact.

The production of such mineral colors as chrome yellow, orange, and green, iron buff, Prussian blue, ultramarine, etc., amounted in 1914 to 2,500 short tons, valued at \$594,000. The increase in the value of the output during the quinquennial period was 52 per cent. There has been no very noteworthy increase since 1914 in the manufacture of these wares, except in the case of ultramarine, for which there had been a considerable dependence upon European sources prior to the war.

A total of 36,000 lbs. of cascara bark were cut on the Siuslaw National Forest in Oregon, during the latter half of last year, according to the Government's foresters. A steady demand for this bark for medicinal purposes, both in the United States and in Europe, is reported to exist. Before the war most of the exported product went to England and Germany.

REVIEW OF RECENT PROGRESS IN ELECTROLYTIC IRON.*

By OLIVER W. STOREY.

Electrolytic iron, up to within the past few months, has been a laboratory rather than a commercial product, but recent developments show that it is another electrochemical achievement to take its place among the industries of this country. At least one of the large electrical concerns is turning out 1,000 pounds (453 kg.) of electrolytically refined iron per week with a probable increase to several times this output in the near future. The method used is that developed by Burgess¹ and later modified by Watts.¹⁵ The electrolyte consists of 150 grammes of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 75 grams $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and 120 grams $(\text{NH}_4)_2\text{SO}_4$ per liter, with a specific gravity of 1.125 at 20° C. Ammonium oxalate is used as an addition agent. The anodes consist of bars of basic open-hearth steel. The deposit reaches a thickness of $\frac{3}{8}$ to $\frac{1}{2}$ inch (10 to 13 mm.) before it is necessary to remove the cathode.

While the electrolytic refining of iron is an infant industry at the present time it is well to remember that electrolytic zinc refining was at the same stage of development a year ago. Two years ago it was thought doubtful whether the problem could be solved except in the distant future. Now we read in the technical press of the erection of electrolytic zinc refineries whose cost will amount to several millions of dollars. With this example before us who can predict what the next few years will accomplish in the electro-deposition of iron?

Electrolytic iron is known to have been produced on a laboratory scale seventy years ago. As long ago as 1860 it was used for the plating of copper engravings for the printing of bank notes at the Imperial Mint at Petrograd, Russia. Until recently the only use to which electrolytic iron had been put was in the so-called "steel facing" of dies and electrotypes. Its hardness, which makes it suitable for such purposes, is due to hydrogen, either occluded or combined.

The commercial production of electrolytic iron as a source of pure iron received a decided impetus in 1904 when Burgess and Hambuechen¹ presented their paper on "Electrolytic Iron" before this Society. They showed that it was possible to refine iron by methods similar to those used for the refining of copper and obtain deposits up to one inch in thickness. The electrolyte consisted of a neutral ferrous sulphate solution containing some ammonium sulphate, while the anodes consisted of slabs of wrought or other soft iron. The current efficiency of deposition was near 100 per cent

*Paper presented at the 29th General Meeting of the American Electrochemical Society held in Washington, D. C., April 27-29, 1916.

¹Burgess, C. F. and Hambuechen, Carl. Electrolytic Iron. Trans. Am. Electrochem. Soc., 5, 201 (1904).

¹⁵Watts, O. P. and L. M. H. The Effect of Addition Agents in the Electro-deposition of Iron. Trans. Am. Electrochem. Soc., 25, 527 (1914).

and the resulting iron was of a high degree of purity, containing less than 0.10 per cent and often under 0.03 per cent of impurities. Over three tons of iron was refined and used for the production of over 1,000 "pure iron" alloys which were tested for their various properties.

After several years' experience upon a semi-commercial scale at the University of Wisconsin, Burgess⁵ gives the following figures on the cost of commercial refining of mild steel, the product being an iron of a high degree of purity. He estimates the power cost per ton at \$10, with power at a cent per kilowatt hour, one kilowatt hour producing two pounds (907 g.) of iron. The cost for labor, solution maintenance and fixed charges is estimated as equal to the power charge or \$10. The anode material is assumed to be a mild steel costing \$35. This would make the total cost about \$55 per ton of refined iron. With power at $\frac{1}{2}$ cent per kilowatt hour this cost would be reduced to \$50.

In 1908 Cowper-Coles² described a method of making finished iron sheets and tubes by electrolytic methods from pig iron or from iron ore, using insoluble anodes when ore was used. The electrolyte was a 20 per cent solution of sulpho-cresylic acid saturated with iron. The method differs from the Burgess process in that pig iron and iron ore are refined, and in a different choice of electrolyte. The process has not been used commercially though it is stated that works are being erected for the manufacture of electrolytic iron by this method.³

A detailed description of the Cowper-Coles process is given by Palmaer and Brinell.⁴ They state that the electrolyte is a concentrated solution of ferrous chloride with additional organic compounds, such as the cresol-sulphonic acids, and enough iron oxide to make a sort of a gruel. The additional iron oxide is used for reducing the acidity and polishing the iron which is deposited as a sheet on a rapidly revolving cathode at a temperature near the boiling point of water. The current density used is about 63 amperes per square foot (7 amp. per sq. dm.). The resulting product is brittle due to the presence of several tenths of one per cent of hydrogen. It also contains about 0.50 per cent of impurities, exclusive of hydrogen, while the pig iron used for anodes contains about 7 per cent. The chlorine content of the deposited iron is high, probably being occluded electrolyte. This is a serious defect as it impairs the mechanical properties and promotes rusting. The figures given by Palmaer and Brinell show that the cost of the electrolytic iron would be from $2\frac{1}{2}$ to 3 cents per pound (453 g.), de-

pending upon the cost of power, though the inventor claims that the cost is below 2 cents.

In 1911 Fischer took out patents⁶ for the manufacture of ductile electrolytic iron in which he claims that ductile iron may be deposited from a hot solution of ferrous chloride if hygroscopic salts, such as the chlorides of calcium, magnesium, or aluminum, are added to the electrolyte. He claims that the ductility of the product increases with the electrolyzing temperatures and that perfectly ductile iron is obtained at temperatures varying between 100° and 120° C. The preferred solution consists of a highly concentrated mixture of ferrous and calcium chlorides, 450 parts of ferrous chloride, and 500 parts of calcium-chloride being dissolved in 700 parts of water. Under these conditions a current density of 180 amperes per square foot (20 amp. per sq. dm.) may be used.

Fischer's method for the production of ductile electrolytic iron is used by the Langbein-Pfannhauser-Werke of Germany for the commercial production of sheets and other articles. Duisberg⁷ states that by this method the iron is deposited free of hydrogen and that its hardness sinks below that of silver and gold, and is not much greater than aluminum.

Ramage⁸ took out a patent in 1911 in which he makes electrolytic iron from iron ore. The ferric ore is dissolved in sulphuric acid and reduced to the ferrous state by sulphur dioxide. The anode compartment of the electrolytic cell is separated from the cathode compartment by a diaphragm. The portion of the electrolyte in the anode compartment is kept saturated with the sulphur dioxide which acts as a depolarizer. The electrolyte in the cathode compartment must be kept free of sulphur dioxide as the nascent hydrogen at the cathode would reduce it, depositing sulphur and contaminating the iron.

Part of the sulphur dioxide is oxidized to sulphuric acid at the anode. Ramage proposes to concentrate this liquor and distill off the acid. In this manner the products are both sulphuric acid and electrolytic iron.

In a later patent Ramage⁹ dissolves iron in a ferric liquor and electrolyzes the resulting ferrous liquor in a cell with a diaphragm and insoluble anode. The ferric liquor and free acids which result at the anode are again reduced and neutralized by the impure iron to be refined. This later operation is carried out in a separate tank and the resulting liquor filtered to keep the liquor clear in the refining tank.

In 1913 Boucher¹⁰ received a patent in which the electrolyte is a solution of one or more ferrous salts, such as the sulphate or chloride. This is stirred in contact with the air before electrolysis to form iron-

⁵Burgess, C. F. Electrolytic Refining as a Step in the Production of Steel. *Trans. Am. Electrochem. Soc.*, 19, 181 (1911).

²Cowper-Coles, S. The Production of Finished Iron Sheets and Tubes in One Operation. *Jour. Iron and Steel Inst.*, 78, 134 (1908).

³Met. and Chem. Eng., 12, 787 (1914).

⁴Palmaer, W., and Brinell, J. A. Electrolytic Production of Iron Sheets and Tubes, etc. *Met. and Chem. Eng.*, 11, 197 (1913).

⁶Fischer, Franz. Process for the Manufacture of Ductile Electrolytic Iron. U. S. Patents 992,551-2, May 23, 1911.

⁷Duisberg, Carl. The Latest Achievements and Problems of the Chemical Industry. *Elighth Int. Cong. App. Chem.*, 28, 86 (1912).

⁸Ramage, A. S. Process of Making Sulphuric Acid and Electrolytic Iron. U. S. Patent 984,703, Feb. 21, 1911.

⁹Ramage, A. S. Electrolytic Method of Refining Iron. U. S. Patent 1,007,388, Oct. 31, 1911.

¹⁰Boucher, A. assignor to Société Le Fer. Process for Making Electrolytic Iron. U. S. Patent No. 1,086,132; British Patent No. 16,565, July 18, 1913; French Patent No. 458,294, Aug. 2, 1912.

oxychloride which reacts with the hydrogen formed at the cathode and therefore acts as a depolarizer. The electrolyte is described as having a clear chestnut brown color and should not foam. During electrolysis, oxidation may be controlled by means of an adjustable opening in the cell cover. To reduce any ferric salts formed the electrolyte is passed over iron shavings in a separate vessel at a speed varying with the current density and with the amount of phosphorus in the cast iron anode. If this amount is one per cent, a circulation of four liters per hour per ampere is suitable. The concentration of the electrolyte is regulated in accordance with the amount of air supplied, but must be maintained constant during working; a suitable density is 35° to 40° Bé. The cathode is rotated at a speed proportional to the current density; peripheral velocities of 100 to 120 meters per minute are suitable respectively for densities of 45 to 72 amperes per square foot (5 to 8 amp. per sq. dm.). The temperature of the electrolyte is raised for high current densities but must not vary during electrolysis; it may be 50° to 75° to 77° C., respectively for densities of 36 and 90 amperes per square foot (4 and 10 amp. per sq. dm.). Iron thus obtained is annealed and is then ready for commercial use.

Reed's patent¹¹ covers both the manufacture of electrolyte iron and the making of sulphuric acid as a by-product. The electrolyte is a solution of iron sulphate. The anode is made of spongy lead which becomes sulphated as the electrolysis proceeds. By this method free sulphuric acid does not form in the electrolyte and there is no tendency for the cathode to dissolve. The resulting lead sulphate is treated electrolytically in a separate receptacle and the sulphuric acid recovered. It is claimed that the electrolytic iron is free of hydrogen.

In 1913 Cowper-Coles¹² obtained a British patent in which he proposes to avoid exfoliation and brittleness in electro-deposited iron by suspending an iron sponge in an electrolyte used for refining iron. He claims to make iron tubes, ingots, sheets or produces pure iron directly from ores. The electrolyte is a concentrated solution of FeSO_4 or FeCl_2 which is electrolyzed, with or without a rotating cathode. As an example he states that a nearly boiling solution containing 1500 grams FeSO_4 per liter is used as electrolyte and under such conditions the current density may be as high as 40 amperes per square foot (4.5 amp. per sq. dm.). The iron sponge may be gotten by roasting a sulphide or other iron ore, with recovery of the sulphur and then reducing by gas.

Guillet,¹³ in a paper before the Iron and Steel Institute in 1914, described the process of the French Company "Le Fer" at Grenoble for making electrolytic iron. This company makes tubes, sheets, and material

to be melted, the raw material being pig iron. A cathode revolving in a neutral solution of iron salts is used, the solution being maintained neutral by the circulation of the electrolyte over the surface of the iron. The bath also receives periodic additions of a depolarizing medium such as the oxide of iron. About 90 amperes per square foot (10 amp. per sq. dm.) is the current density used.

An iron having the following average analysis is claimed to be produced after removing the gases:

	Per Cent.
Carbon	0.004
Silicon	0.007
Sulphur	0.006
Phosphorus	0.008

Guillet states that it is possible to guarantee phosphorus lower than 0.010 per cent. When a current density of 90 amperes per square foot (10 amp. per sq. dm.) is used the yield per kilowatt-year is two tons of metal, including cost of power for accessory service. The iron is annealed at 900° C. after which it possesses a high degree of ductility and can be readily worked. The current density used would depend upon the cost of power. By using a current density of 45 amperes per square foot (5 amp. per sq. dm.) instead of 90, four tons of iron may be produced per kilowatt-year instead of two as the voltage drops one-half. Where the cost of power is high the current density should be low to secure higher efficiency. Guillet estimates that the total cost would be from \$30 to \$40 per ton in France according to locality. The cost in the United States would probably be near \$50 owing to higher cost of power, labor and materials.

The process described by Guillet is similar to that described by Cowper-Coles.²

The various processes described for the production of electrolytic iron vary from the simple one used by Burgess to the complicated process of Boucher. While the more complicated methods use the cheaper pig-iron and iron ore as sources of raw material, it is doubtful whether the cost of the finished iron is much less than in the simple refining process. The cost of rotating cathodes, removing slimes, solution maintenance, auxiliary apparatus, and the necessity of careful chemical regulation of the electrolyte minimize the advantage of low cost of raw material.

USES FOR ELECTROLYTIC IRON.

Electrolytic iron when deposited by the usual methods is brittle, due to the hydrogen present. In this form it can be easily broken into small pieces and even ground into a powder. By heating the iron to a red heat the hydrogen is driven off and the iron becomes ductile, the ductility increasing with the temperature of annealing.

Brittle electrolytic iron as deposited is highly soluble in acids,¹⁴ being much more readily soluble than zinc. Annealing the iron makes it become more resistant to acid attack than ordinary irons and steels.

¹¹Reed, C. J. Electro-deposition of Iron. U. S. Patent No. 1,055,653, March 11, 1913; German Patent No. 269,927, April 25, 1912.

¹²Cowper-Coles, S. Manufacture of Electrolytic Iron. British Patent No. 12,683, May 31, 1913.

¹³Guillet, L. Electrolytic Iron: Its Manufacture, Properties and Uses. Jour. Iron and Steel Inst., Oct., 1914; Iron Age, 94, 1290 (1914); Met. and Chem. Eng., 12, 787 (1914).

¹⁴Burgess, C. F., and Engle, S. G. Observations on the Corrosion of Iron by Acids. Trans. Am. Electrochem. Soc., 9, 199 (1906).

This property of the brittle iron has resulted in the suggestion that it be used for the manufacture of hydrogen by acid attack in place of zinc and other forms of iron.

The brittleness of the iron and its purity make it an ideal material for melting in crucibles, the hydrogen content having the additional virtue of forming a reducing atmosphere. The brittleness also allows it to be readily broken into small pieces for introduction into the crucible.

The high purity of the iron makes it possible for it to be used in competition with Swedish iron and at approximately the same cost.

It may also be used for pharmaceutical purposes as a base for compounds of which iron is a constituent. Here again its purity is of value.

The much suggested use of electro-deposited iron for electro-magnetic purposes appears to be becoming of commercial importance. While the magnetic qualities of electrolytic iron seem to be superior to the commercial silicon irons its high electrical conductivity counteracts this favorable property.

Electrolytic iron also is used as a basis for scientific experimental work on the various properties of iron where the purest available iron is needed to secure the most accurate data. It is also used as a basis for "pure iron" alloys.

The materials that have been produced and which seem to give the most promise for direct production without further mechanical working are sheets and tubes. By producing these directly by deposition in such a manner as to not require further operations it would be possible to make thin sheets and tubes of great uniformity. In tubes having thin walls made by mechanical processes, these often vary in thickness and it is hoped that this defect will be overcome by making them electrolytically.

EFFECT OF ADDITION AGENTS UPON THE DEPOSITION OF IRON.

The effect of addition agents upon the electro-deposition of iron has been studied by Watts and Li.¹⁵ The solution used for experimental work contained 150 grams of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 75 grams $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 120 grams $(\text{NH}_4)_2\text{SO}_4$ per liter with a specific gravity of 1.125 at 20° C.

The addition agents giving the best results are given in the following table in order of excellence (amount given is per liter):

- 6.0 grams ammonium oxalate.
- 0.6 gram formin or hexamethylenetetramine.
- 2 drops phenol.
- 4 drops formalin.
- original solution.

These results show that the deposition of electrolytic iron may be improved by addition agents.

DETAILED ESTIMATE ON COST OF ELECTROLYTIC IRON.

The appended data covering in detail the cost of producing electrolytic iron on a large scale has been kindly furnished by Mr. C. F. Burgess. The plant is

assumed to be 1000 kilowatt capacity with an output of 8,640 tons per year of 360 days.

A current density of 10 amperes per square foot (1.1 amp. per sq. dm.) is assumed and an energy consumption of one kilowatt hour for every two pounds of iron is also taken as warranted by past experimental work.

The most suitable anode material would probably be the crop ends of very mild steel, preferably the product of a basic open-hearth furnace, or even better from concerns which are making the newer higher purity irons. These materials would have the advantages of low phosphorus and manganese and also of the other elements, which should have the least tendency towards sliming and consequent deterioration of the electrolyte.

It probably could be purchased at an average of \$15 per ton and would be worth \$20 per ton rolled into a form needed for use in the refining tanks. This figure would cover also the freight charges to the plant.

The estimate of Table II shows a total investment of \$128,360. This does not cover the total capital required. It does not include, for example, real estate investment other than that involved in \$1 per square foot (0.1 sq. m.) of building space; it does not provide for working capital or accumulated stock, nor does it provide for development work which would be necessary.

Table III gives the principal items of operating cost, which show that a figure of about \$10 per ton of refined iron is possible. In fact, this is believed to be a liberal estimate. It is larger than the figures given for the refining of copper, and in all probability the cost of refining iron would not be materially greater than that of refining copper. The operating costs, however, do not include interest on investment.

The cost of raw material is taken at \$20 per ton, thus making the cost of the electrolytic iron approximately \$30. If it would become necessary to use a low phosphorus rolled stock worth \$30 a ton the cost would be increased 33 1/3 per cent, which would limit the use of the refined iron.

TABLE I.

Estimate on Electrolytic Iron Plant.

Power consumed in tanks.....	1,000 kw.
Output, refined iron. 24 tons per day (8,640 tons per 360 days)	
Refining Tanks—	
Made of 2-inch (5 cm.) cypress lumber, re-inforced.	
Size, 6 ft. 6 in. (200 cm.) long; 3 ft. 6 in. (105 cm.) deep;	
3 ft. 8 in. (110 cm.) wide, outside.	
Number, 840.	
Floor space per tank, 50 sq. ft.	
Total floor space, tank room, 42,000 sq. ft.	
Cost of each tank—	
Lumber, 190 ft., at 5 cents.....	\$ 9.50
Labor and re-inforcement	9.50
Fittings, drains, pipings, and conductors	11.00
	\$30.00

Amount of iron in each tank—

11 anodes 3 ft. (90 cm.) x 2 ft.	
(60 cm.) x 1 in. (2.5 cm.)	
thick =	2,530 lb. (1,150 kg.) per tank
10 thin sheet cathodes.....	70 lb. (32 kg.) per tank
	2,600 lb. (1,182 kg.) per tank

2,600 lb. at 1 cent = \$26.00.
Electrolyte, at 33 cents per cu. ft. = \$23.00.

TABLE II.

Cost of Electrolytic Installation.

840 tanks, with fittings, at \$30.....	\$ 25,200.00
Electrolyte 840 x \$23	19,320.00
Iron under treatment—	
840 x 2,600 lbs. = 1,092 tons at \$20.....	21,840.00
Total cost of tanks	\$66,360.00
Cell room—42,000 sq. ft. (3,800 sq. mi.) floor space. \$	42,000.00
Additional equipment—	
Traveling cranes, pumps, storage tanks, purifying tanks, etc.	20,000.00
Total investment inside switchboard	\$128,360.00

TABLE III.

Operating Costs.

Power, delivered to cells, 1,000 kw. at \$50.....	\$50,000.00
Engineering and superintendence	7,000.00
Labor, 20 men at \$800 per annum.....	16,000.00
Depreciation—	
Tanks and fittings: 15% on \$25,200.....	\$3,780.00
Electrolyte: 10% on \$19,320	1,932.00
Iron under treatment: none.....	
Building: 5% on \$42,000	2,100.00
Accessories: 10% on \$20,000	2,000.00
	9,812.00
Miscellaneous repairs, etc.	10,000.00
	\$92,812.00
Total cost of 8,640 tons =	\$92,812.00
Total cost per ton =	\$10.75

METHOD OF ESTIMATING AMMONIA.

The following method of estimating ammonia was described by G. E. Foxwell in the English paper, *The Gas World*:

The method is based on a colorimetric reaction discovered by Berthelot sixty years ago. If excess of phenol and a little sodium hypochlorite are added to a solution of ammonia or its salts, a blue coloration is produced. As a qualitative test it is extremely sensitive, less than one-ten-thousandth of a milligram of ammonia giving a distinct coloration. Thomas has pointed out the possibility of using this reaction as a quantitative test, but somewhat meager details were given.

Desiring a rapid method of estimating ammonia in waste liquor, the writer has gone into this test thoroughly, and has determined the conditions necessary to make the reaction quantitative.

The test is carried out as follows: Pure ammonium chloride is prepared, 0.063 gramme dissolved in distilled water and the solution made to one litre. Thirteen test tubes of as nearly as possible equal bore are taken, and varying amounts of NH_4Cl solution run in from a burette. In the first test tube is placed 0.1 c.c. of this solution, into the second 0.3 c.c., into the third 0.5 c.c., then 0.7 c.c., 1 c.c., 1.5 c.c., 2 c.c., 2.5 c.c., 3 c.c., 3.5 c.c., 4 c.c., 4.5 c.c., 5 c.c. Then each test tube is made up to 5 c.c. with distilled water. To the solutions thus prepared 1 c.c. of a 4% solution of phenol and 1 c.c. of dilute solution of sodium hypochlorite are added.

It is necessary to heat the solution before any blue coloration appears, and everything depends on the

mode of heating. Thus if the test tube is heated to boiling slowly over a small flame, the coloration is much more intense than if heated quickly. In order to ensure that each experiment shall be under the same conditions, it is advisable to immerse the tubes in a beaker of boiling water for at least $1\frac{1}{2}$ minutes, which will be sufficient to bring out the full color.

It does not seem to make any difference in the color if this heating in boiling water is continued for some time. It is important to note that when the phenol and hypochlorite have been added no ammonia is evolved by boiling the solution, even if the ammonia was present in the first place as hydrate (NH_4OH).

The specimen tubes thus made up and colored by immersion in boiling water appear to keep their color indefinitely.

In order to test a sample of waste liquor for total ammonia, 5 c.c. are taken and made up to 300 c.c. with distilled water. Five c.c. of this solution is pipetted into a test tube, and 1 c.c. of 4 per cent phenol solution, together with 1 c.c. dilute sodium hypochlorite. The mixture is heated in boiling water as before, cooled under the tap, and the color compared with the thirteen standard tubes. If the proportions of both free and mixed ammonia are desired, 5 c.c. of the liquor are boiled to expel free NH_3 , and the solution is then made up to 300 c.c. and treated as before.

It may seem hopeless to expect a color test to be of any use in connection with the waste liquor, but at the dilution employed the coloration is so slight as to be negligible.

For simplicity, the following table is given showing the percentage of ammonia in waste liquor, assuming every operation to be carried out exactly as detailed above:

c.c. standard NH_4Cl solution in tube	0.1	0.3	0.5	0.7
Per cent NH_3 in liquor.....	0.0024	0.0072	0.012	0.0168
	1.0	1.5	2	2.5
	0.024	0.036	0.048	0.06
	3	3.5	4	4.5
	0.072	0.084	0.096	0.108
				0.12

It was found that free acid must not be present, or the test fails. Free lime has no influence.

COMPARATIVE RESULTS.

	(1)	(2)	(3)
	Per Cent.	Per Cent.	Per Cent.
Ammonia by color	0.010	0.052	0.026
Ammonia by distillation	0.012	0.050	0.025

The test is not as accurate for ordinary works purposes as a distillation, but is exact enough to show at a glance how the stills are working, as, if the solutions are made up ready, only three or four minutes are required for the test.

For the estimation of larger quantities of ammonia, the writer would not recommend this method, as owing to the great dilution required any error is considerably magnified. Thus the percentage of ammonia in a liquor was estimated by the color method as 1.88 per cent, whereas by distillation only 1.77 per cent was found.

RECENT PROGRESS IN FLOTATION.*

By ROBERT J. ANDERSON.†

INTRODUCTION.

One of the most marked and revolutionary advances of recent years in the art of concentrating ores is the advent and application of the flotation process. Although the basic and essential principles of flotation had been disclosed by the early work of Haynes, Everson, and the Elmore brothers, it is only within the last decade or so that the process has been a commercial success. Historical considerations point out the fact that the instillation of the Delprat process, in 1903, at the Broken Hill Proprietary mine in Australia, was probably the first important commercial application of any flotation process; some other installations were also made at or about the same time. Flotation as practised today is the result of the diligent labor of many men, and the present state of development cannot be ascribed to any one individual. In its early stages the flotation process of concentration was decidedly uncertain of success because of certain inherent difficulties which were to be overcome. At present every mill owner in the country is considering its applications. The froth flotation process is markedly efficacious in extracting the mineral sulfides from slimes, and, in the main, is more or less restricted to the treatment of extremely fine material.

In a general way, there are three divisions into which the flotation processes may be separated; namely (1) film flotation, (2) bulk-oil flotation, and (3) froth flotation. Further, these three classes blend into one another gradually, according to the patents secured for the different processes. Technical distinctions are based on such points as there, viz., acid, neutral, or alkaline pulp solutions; mill temperature or hot solutions; various secondary apparatus employed for the introduction of air or the production of gas bubbles; amounts of oil; and other minor differences almost *ad infinitum*. The more important processes which have so far survived elimination by litigation or other means include the following: Minerals Separation process; Potter-Delprat process; De Bavay process; Callow pneumatic process; Hyde process; Janney process, and the Macquisten tube process; and, further, the preferential processes—Murex, Lyster, and Horwood. These processes have been described at length in the patent literature, in the scientific press, and elsewhere, and further comment would make this writing unnecessarily cumbersome.

Strictly speaking, the subject of flotation naturally falls into two divisions, to wit, legal disputes and technology. Litigation has undoubtedly been the most active, as well as destructive, movement in the field, for the development of the process has been constantly attended with an unwholesome amount of legal differences among the contending interests. Probably there

was never a technical achievement so hotly contested in the courts as this one. All these involved disputes have so distinctly retarded progression in this process that, charitably speaking, flotation is today in a chaotic state.

Regarding present operations, although there are so many flotation plants at work, there is a decided dearth of available data. In short, actual results have not found their way into the literature devoted to mining and allied subjects, presumably on account of the veil of mystery which is supposed to, and actually does, hang over the process. Practice varies with the locality, and, as a whole, the methods are in no sense standardized. Development at the present time is being retarded on account of certain cases pending in the courts, which involve the Minerals Separation, Ltd., and others. For, with these cases still to be adjudicated, many operators seem to hold that any attempt at development and standardization would be folly, which would incur a certain waste of time and money, should the decision be rendered in what is considered the unfavorable way.

PROGRESS IN VARIOUS LOCALITIES.

Australia.

To all intents and purposes Australia is in the van in flotation at present, and has been since the advent of the process. The first important flotation installation was that of the Delprat process, as mentioned in the foregoing; this mill operated successfully from its inception and has continued to do so. The joint Potter-Delprat process was also applied to the treatment of ore at the Broken Hill Proprietary Block 14 Company's mine in 1903, but ceased operations in 1905; whether this particular plant ever recommended operations is not known to me. These installations, however, mark the beginning of the remarkable growth in the zinc industry of Australia, which country now produces one-fifth of the world's supply of spelter. The Potter-Delprat process is peculiarly adapted to Broken Hill ores, and this fact is the main reason for its marked success; on other ores it may not be as efficient as some of the other processes.

The Minerals Separation process, licensed by the Minerals Separation, Ltd., and the Minerals Separation American Syndicate, Ltd., was first employed about 1904-05 by the so-called Sulfide Corporation in Australia. In brief, the process then was an adaptation of the Cattermole patent, the principle of operation being the coagulation and sinking of the mineral sulphides with a large amount of oil. The original idea of Cattermole was abandoned in 1905 and true froth flotation adopted. The Minerals Separation process was practised in 1907 at the Central mine at Broken Hill, and has operated successfully to date, producing zinc concentrates. At the same time the Minerals Separation, Ltd., by right of purchase secured a large tailing dump from the Sulfide Corporation; the Minerals Separation process was applied to the concentration of the material, and the mill was an

*From Journal of the Franklin Institute.

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immediate success, producing good concentrates. During this time flotation was subjected to rigid experimentation throughout the Broken Hill district, and the practicability of the process was satisfactorily demonstrated. Minor improvements made from time to time have brought it to its present state of perfection.

It is a noteworthy fact that the introduction of flotation at Broken Hill resulted in the total scrapping of the electric separating machines, all being renounced because the newer process effected an extraction of from ten to twenty per cent more zinc. Previous to the introduction of the Horwood process, it had been impossible to successfully separate the lead and the zinc in the flotation concentrates into marketable products. Owing to the slimy character of the concentrates delivered by the flotation units, the method of further treatment on tables was an imperfect one; this handling was practised, however, as none other so good was available.

The Zinc Corporation, Ltd.,¹ by reason of extensive experiments with the Horwood process, has definitely adopted it as a preferential method of separating the zinc and lead sulphides in the slime concentrates. Briefly, the Horwood process involves a partial sulphatizing roast of the material to be treated, which coats the lead sulphide particles with $PbSO_4$, while the other sulphides of the ore, zinc, iron, and copper, are not so affected. The galena is thus "deadened," and the sphalerite may be floated in the ordinary manner in a Minerals Separation or other flotation machine. According to a report of the Zinc Corporation,² the Horwood process is a practical installation at its plant. Figures from the most recent annual statement show that the lead flotation plant treating tailings from other companies' mines and also ore from the Zinc Corporation South Block mine produced 26,567 tons of lead concentrate assaying 64.6 per cent Pb, 6.45 per cent Zn, and 9.2 ounces Ag from 141,667 tons of ore assaying 14.4 per cent Pb, 9.3 per cent Zn, and 2.6 ounces Ag. The zinc flotation plant for the same period treated 221,620 tons of tailings assaying 13.68 per cent Zn, 5.93 per cent Pb, and 6.42 ounces Ag, yielding 63,300 tons of zinc concentrates assaying 43.96 per cent Zn, 13 per cent Pb, and 13.91 ounces Ag. Of the original material treated in this latter plant, 169,180 tons were dump tailings and the remainder was from the lead plant mentioned above and the British and Junction mines. The Horwood process plant in the same time yielded 5,822 tons of zinc concentrates assaying 48.1 per cent Zn, 6.80 per cent Pb, and 16.90 ounces Ag; and 2,619 tons of lead concentrates assaying 35.55 per cent Pb, 1.40 per cent Zn, and 40.52 ounces Ag. The material treated in the process just mentioned included 6,144 tons of zinc slime from the zinc plant and 3,169 tons from the accumulated dumps for a return as indicated. The

cost of operation of the Horwood plant was 30 cents per ton of ore.

A Minerals Separation plant was started in July of 1911 at the Kyloe Copper mine in New South Wales. The flotation yields a 22.65 per cent copper concentrate from low-grade ore with an extraction of 86.36 per cent.

Experiments³ made in 1913 at Mt. Morgan, Queensland, resulted first in the erection of a 300 to 400 ton-per-day experimental Minerals Separation unit. The ore contained about 2 per cent Cu as chalcopyrite and \$6 in gold per ton. Tests in the experimental unit were satisfactory, and the erection of a 1,000-ton plant followed. The work on this cupriferous gold ore showed that all ore had to pass 60-mesh, or good extraction could not be had; and up to 120-mesh the extraction increased in proportion to the fineness of the grinding.

The Elmore Vacuum Oil process was tried by the Zinc Corporation at Broken Hill and later discarded in favor of the Minerals Separation process. The Elmore Vacuum process is not finding much application today; most of the installations are in Europe or the British Isles. The so-called De Bavay process was secured by the Minerals Separation, Ltd., in a merger of interests. The De Bavay process is pre-eminently fitted for the treatment of sands, the tailings or other products to be floated being first deslimed. It will effectively treat material through 30-mesh and not over 5 to 10 per cent of slime, which is much coarser than the Minerals Separation process can successfully cope with. For fine material, *i. e.*, slimes, the latter is eminently suited, while the De Bavay process is not so efficient.

Work at the Whim Well in western Australia with the ingenious Murex process demonstrates that this preferential method has potentialities; and its future probably lies in the concentration of cupriferous carbonates or other oxidized ores. Another preferential process which was developed in Australia is the Lyster process, owned by the Minerals Separation, Ltd. This process was worked out in detail at Broken Hill, at the Zinc Corporation plant, and received favorable consideration from that company for some time previous to the present great war.

The importance of Australia today is due in great measure to flotation, for in less than a decade Australia has risen to the position of furnishing one-fifth of the world's supply of zinc. No mining camp in the world produces so much zinc as Broken Hill. The first shipment of zinc concentrate in 1903 from that place was 50 tons; in 1911, 470,000 of 47 per cent grade zinc concentrate were produced by flotation methods.

Arizona.

Flotation has gone forward rapidly in Arizona in the last few years, and there is at present great activ-

¹Mining and Engineering World, Jan. 2, 1915, p. 13.

²Mining and Scientific Press, July 17, 1915, p. 91.

³Mining and Scientific Press, June 27, 1914, p. 1044.

ity in that state because of recent large installations. A noteworthy flotation plant⁴ is that of the Inspiration Copper Company, near Miami, Ariz. At this place there are available some 100,000,000 tons of a 1.63 per cent copper ore, the copper being mostly in the form of chalcopyrite and containing about 0.20 per cent copper as silicate and carbonate. A large amount of experimental work was first performed previous to the erection of the present mammoth mill. The Minerals Separation process, Callow process, Towne-Flinn process, a process devised by D. Cole, of Morenci, Ariz., and a so-called Inspiration process were tried. The first Minerals Separation unit was ready for work in December of 1913, but commencement of operations was retarded on account of power failure; this plant was designed for a capacity of 600 tons per day. The Inspiration process was designed by the metallurgists in charge and was intended to embody the best features of the other machines without infringing on any of the patents except those of the Minerals Separation, Ltd. The Inspiration Company is licensed to operate under the patents of the latter. The present new mill⁵ has a capacity of 7,500 tons daily, and when the entire plant is in operation will have a capacity of some 14,000 to 15,000 tons. In addition, the experimental unit is still operating.

The introduction⁶ of the flotation process, together with some minor changes in the mill of the Consolidated Arizona Smelting Company, resulted in an increased copper recovery of 20 per cent. The ore contains 2 per cent of copper as chalcopyrite, with pyrite in a schistose and quartzitic gangue. The former mill system was necessarily complicated because of the nature of the ore; the chalcopyrite, being of a friable nature, caused heavy losses, but the pyrite was more easily concentrated, as it broke coarsely. Although the same ore, the one from the Blue Bell and De Soto mines, is being worked, the flotation process has ameliorated the heavy losses and is effective where concentration on tables was not. In September, 1915, flotation was responsible for a recovery of 240,000 pounds of copper concentrates, about 70 per cent of the total. This company was among those which first used the Minerals Separation process in the United States. An 11-cell unit with a capacity of 225 tons per day has been installed, and the flotation is consummated in no-acid solutions at mill temperature. The concentrates are not re-cleaned. The oil combination which was found most effective consists of about two parts of wood creosote to one part of a cheap stove oil (light burning oil). The cost of operation is about 27 cents per ton, of which the oil expense contributes 0.028 cent.

The Magna Copper Company⁷ at Superior and the Duquesne Mining and Reduction Company at Duquesne have installed the Callow pneumatic flotation

process. The invention of Callow⁸ marks one of the most distinct advances ever made in flotation. This process calls for agitation with air in an acid, neutral, or alkaline solution, with oil as selective and frothing agent. At Superior the tailings from the finishing tables receive flotation treatment. There are flotation units in experimental operation at the Copper Queen Consolidated Mining Company's mill at Bisbee. Other flotation plants in Arizona include those of the Ray Consolidated Copper Company at Hayden and the plant at the Old Dominion mine. The flotation work of the Miami Copper Company at Miami has become involved in litigation with the Minerals Separation, Ltd.

Idaho.

Flotation has become an important metallurgical process in the Cœur d'Alenes and elsewhere in Idaho. The Callow pneumatic process was applied to the treatment of ores at the mill of the National Copper Company at Mullan, Idaho, the plant being started April 10, 1914. This was the first Callow plant ever erected and was an instantaneous success. Since that time the pneumatic process has been adopted by nearly all the other mines treating lead and lead-zinc ores in the Cœur d'Alenes, notably the Caledonia, Bunkers Hill and Sullivan, Gold Hunter, Morning, Hercules, and others. The plant erected by Callow for the National Copper Company had eight regular rougher cells and two cleaner cells, treating some 500 tons in 24 hours with a consumption of as low as 0.13 pound of refined pine oil per ton. The Callow scheme finds favor in the district for the flotation of slimes and fine sand.

The surface tension tube of A. P. S. Macquisten, patented in 1904, was adopted by the Federal Mining and Smelting Company for operation at its Morning mill at Mullan in 1909. The operation at this place had been fairly satisfactory, but, as the capacity of a single cell is low and as the process is not well adapted to the treatment of slime, froth flotation is more to be recommended.

The new plant of the Hunter Mining Company⁹ at Mullan, according to recent figures, was destined to pay for itself in about three months' time. Under the old scheme of concentration the mill recovery was only 50 to 60 per cent; with flotation as an adjunct the mill is recovering 90 per cent. The flotation process at this place consists of nine Callow rougher machines and three cleaners. Four roughers and two cleaner cells were working in March, 1915, producing from 15 to 16 tons of a 50 per cent lead concentrate from 160 tons of feed. The oil consumption was low, about 0.33 pound per ton.

Montana.

One of the most remarkable and efficient flotation plants in the country is that of the Butte and Superior mill at Butte, Mont., operating on a lead-zinc ore.

⁴Mining and Scientific Press, July 3, 1915, p. 7.

⁵Mining and Engineering World, Jan. 1, 1916, p. 1.

⁶Metallurgical and Chemical Engineering, Dec. 1, 1915, p. 897.

⁷Mining and Engineering World, Sept. 11, 1915, p. 405.

⁸Bull. A. I. M. E., Dec., 1915, p. 2321.

⁹Mining and Engineering World, March 6, 1915, p. 460.

The early experiments of James M. Hyde, conducted at Basin, Mont., led to the introduction of flotation at the Butte and Superior mill. A 1,000-ton-per-day plant is working on the treatment of a zinc middling product as an adjunct to concentration with tables and other mill apparatus. The original recovery was only 60 per cent, but with the flotation end of the scheme operative this has been increased to 91 per cent and more. This mill now uses the so-called Janney frothing machine, and for that reason the company is involved in legal controversy with the Minerals Separation, Ltd., the latter holding that the Janney cells infringe the Minerals Separation patents. No decision has as yet been rendered.

In this flotation process the pulp passes through agitators and thence to a bank of five flotation machines operating in parallel. The first rough concentrates are recleaned, and also the first tailings; a system of *clean* and *reclean* operates with the production of clean concentrates, a middling product, and tailing; the middling is returned to the system. The 55 flotation machines are supplied by six agitators through a distributing system. The frothing is performed in mill temperature solution with pine oil as the collecting element; copper sulphate and sulphuric acid are also added.

A notable installation, also, is that at the Timber Butte mill,¹⁰ which receives ores from the Clark Elm Orlu property. Analysis of this ore shows 20 per cent Zn, 1.5 to 2.5 per cent Pb, 0.8 per cent Cu, 7 to 8 ounces Ag, and 20 to 80 cents in gold. The mill process is a combination of water concentration and flotation. The coarse flotation concentrates are treated on tables in order to remove the lead and iron and produce a marketable product. Mill slimes from an Akens classifier are settled in a Dorr thickener tank, and the prepared pulp then fed to the flotation units. The flotation process is that licensed by the Minerals Separation, Ltd.; there are 8- and 11-cell machines with 150 tons and 600 tons capacity respectively. Recovery has been as high as 98 per cent. The average daily production consists of 110 tons of zinc concentrates, and also lead concentrates of a 50 per cent grade carrying considerable silver.

Another plant, in partial operation, is the 800-ton-per-day plant of the East Butte Copper Mining Company. The Janney type of frothing machine is in use for the treatment of second-class ore and dump tailings.

The large plant recently constructed by the Anaconda Copper Mining Company at Anaconda,¹¹ Mont., is a noteworthy development in this state. The old mill is being remodelled and the flotation process being added to each of the mill sections; each section has a capacity of 2,000 tons of feed per day. Each section of the flotation plant has four Minerals Sepa-

ration machines, 15-cell type; the froth from these machines was cleaned in six Callow pneumatic cells, but the pneumatics have been abandoned and only one clean concentrate is now made. The reagents used in the flotation are: about 6 to 8 pounds of 50° B. sulphuric acid per ton of feed, plus 2 to 3 pounds of kerosene-sludge acid, and 0.5 to 1 pound of wood creosote. Part of the wood creosote is added to the Hardinge grinding mills, and the remainder to the Minerals Separation units. The pulp is heated to about 70° F. The flotation concentrate is thickened in Dorr tanks and dried in Oliver filters.

Utah.

The flotation work in Utah centers about the United States Bureau of Mines and the General Engineering Company in Salt Lake City. The experimental work at the Bureau of Mines, under the direction of Mr. Dorsey A. Lyon, has contributed much to the scientific knowledge and working technic of the process. A new mill has been installed by the Utah Leasing Company¹² at Newhouse, Utah; this is a 500-ton plant, built to treat about 1,000,000 tons of tailings from the Old Cactus mine. The ore is fed to Hardinge pebble mills connected in closed-circuit with Dorr Simplex classifiers; 65-mesh material is treated in the Minerals Separation flotation machines. The oil, most of which is added to the Hardinge mill to get the benefit of the resulting agitation, is a coal-tar cresote—Barrett No. 4—combined with a kerosene acid-sludge from Nicols, Calif.; this oil gave the best results.

Elsewhere.

In California the plant of the Engels Copper Mining Company¹³ is operating under Minerals Separation patents and licenses. This plant is interesting, as it is the only one in which no other process than flotation is used. The ore was not amenable to ordinary wet concentration, but is being successfully treated by flotation. A 12-cell Minerals Separation plant with a capacity of 150 to 200 tons per day is producing a 40 per cent copper concentrate from a mill feed averaging less than 4 per cent Cu. The flotation feed is of considerable fineness—65 per cent of it will pass 150-mesh and only 5 per cent remains on 100-mesh. The oil consumption is low—about 0.4 pound per ton of ore; half of the oil is fed to the tube mill and the remainder to the cells of the frothing machines. The recovery exceeds 84 per cent. The concentrates containing from 10 to 12 per cent moisture are shipped to the Garfield smelter near Salt Lake City. Another California installation is the mill of the Mountain Copper Company at Keswich; this mill is using the Minerals Separation process and has a 250-ton capacity.

That flotation has penetrated the Orient is shown by the plant of the Mitsui Mining Company¹⁴ at its Kamioka mine in Japan. This mine has a yearly output of some 10,000 tons of an ore averaging 10 to 16 per cent

¹⁰Mining and Engineering World, Jan. 1, 1915, p. 29.

¹¹Mining and Scientific Press, Aug. 28, 1915, p. 312.

¹²Mining and Scientific Press, Dec. 11, 1915, p. 889.

¹³Ibid., July 31, 1915, p. 167.

¹⁴Mining and Scientific Press, Sept. 4, 1915, p. 347.

Zn and 3 to 4 ounces Ag. The concentrating plant produces an argentiferous lead concentrate, a zinc concentrate, and a zinc middling; this latter receives treatment by flotation. At this place an acidulated (H_2SO_4) solution is kept at 80° to 85° C., into which a heavy oil is introduced with a pulp ratio of 2 to 1; 29 pounds of 54° B. H_2SO_4 are used per ton. The best recoveries have been obtained on fine material; i. e., 50- and 100-mesh.

The main amount of work with flotation in Nevada has been experimental and has been done at the mill of the Nevada Consolidated Copper Company, embodying mainly the practice of the Inspiration and Ray Consolidated plants already referred to. This work having not progressed further than the experimental stage as yet, no data are available. In New Mexico, flotation processes have been added to the plants of the Chino Copper Company at Hurley, using Janney machines, and at Tyrone, where the Burro Mountain Copper Company has determined the amenability of its slimes with a 500-ton mill and is now constructing a 1,000-ton plant. At Chewelah, in Washington, the United Copper Mining Company has a flotation plant in successful operation on slimes.

Flotation¹⁵ has been an active factor in the mining industry of Colorado for a few years, and flotation plants are in operation at such places as the Hudson mill and Newton mill at Idaho Springs, the Sunnyside mill at Eureka, Gold King Leasing Company at Silverton, and others too numerous to mention. In Tennessee, plants are in operation at Ducktown and at the Mascot mill of the American Zinc, Lead, and Smelting Company. This company is about to enter more actively into the field, particularly in Joplin, Mo. A Minerals Separation process has been practiced at Britannia Beach, British Columbia, by the Britannia Mining and Smelting Company. The plant of the Braden Copper Company at Sewell, Chile, South America, is an 8-cell Minerals Separation process floating copper sulfide.

OILS IN FLOTATION.

The importance of oils¹⁶ in flotation work can scarcely be overestimated, since most or all of the different processes have come to the use of oils. Since almost any kind of oil may be used to effect a separation of the finely-divided sulfides from the gangue, it is not surprising that the number of different oils, which have been tried experimentally and commercially, is almost without end. The present tendency is to determine by trial a suitable oil mixture for a given ore. It is found that coal-tar products are particularly efficacious in the flotation of copper ores, but are not so good for lead and zinc. In the flotation parlance, oils are divided into two kinds; namely, (1) frothing oils and (2) collecting oils. There may be a further classification of each of the above into such types as mineral oils, animal oils, and vegetable oils. One oil in itself may combine both the properties of collecting

and frothing, so that at times there may be difficulty in stating whether an oil is a frothing oil or a collecting oil.

1. *Frothing Oils*.—A number of oils have been successful frothing oils, and this includes the pine oils—steam refined and crude—cresylic acid, and turpentine and other pyroligneous products from the distillation of woods. The coal-tar phenols and most or all of the essential oils are efficient frothers. The essential oil of the *Eucalyptus globulus* finds wide application as a flotation oil in Australia on account of low cost; it would be prohibitively costly to use it in this country. Pine oil is unquestionably the best frothing agent known, but has recently become prohibitively costly, and the same is true of cresylic acid. In general, the essential oils give a coherent froth and satisfactory extraction.

2. *Collecting Oils*.—The mineral and tar oils have a marked selective action on the mineral sulfides and are generally poor frothers. The mineral oils used in flotation include crude petroleum, refined oil, gasoline, kerosene, creosol, and coal tar and coal tar creosotes. Oils derived from the destructive distillation of woods, such as wood creosotes, pyroligneous acid, and similar products, are good flotation oils from the standpoint of cost and efficiency. Coal tar has the property of stiffening a weak froth, and may be employed as a mixture with 10 per cent pine oil.

Recent commercial practice demonstrates that acid may be eliminated from the pulp solutions if a suitable oil mixture be determined. The same results can evidently be obtained in an alkaline or neutral pulp as in an acid one. The flotation experts employed in the erection of plants have come to the practice of using, in the work at hand, the oil available. An instance is given where power is generated at a certain plant using Deisel engines, and the practice has become so fixed now that the same oil is used for flotation as is used in the Deisel equipment. Evidently no given oil or combination of oils will perform effective work on all ores; it is a particular problem for each ore to find the most suitable oil mixture.

It is the conviction of at least one large company supplying oils for flotation consumption that there are too many oils on the market, and that a medium-price oil (20 cents per gallon in tank cars) will be the frothing element which large consumers will favor. It is the consensus of opinion that pine products are essential to the production of good froth, and are also good selective oils. Considerable difficulty is experienced by the consumers in the duplication of orders, for it seems as though the oil companies cannot or do not furnish the same oil on repeated orders. Why this condition of affairs should obtain is not apparent.

MISCELLANEOUS CONSIDERATIONS.

The present practice favors the ball mill for grinding the tailings or other material to be floated, as the

¹⁵Mining and Engineering World, Jan. 1, 1916, p. 1.

¹⁶Mining and Scientific Press, Sept. 25 and Dec. 4, 1915.

bulk of the feed is thus reduced to slime, which is the ideal feed for froth flotation. The use of Dorr thickening tanks for thickening the pulp, placed in closed circuit with the grinding mill, seems to be a present tendency for a future standard practice. The fact that flotation can and does work best on slimes has removed the old dread of mill operators for making slimes in the wet concentration; this will result in some minor changes in mill practice. Before shipment to smelter or other market, flotation concentrates must be dewatered by filters to a moisture content of about 8 to 10 per cent; otherwise, heavy freight bills are incurred which might consume the profits. The moisture content cannot be too low in the case of long shipments, or heavy dusting losses will take place. The so-called Oliver filter will reduce the moisture to 8 per cent or less, and is preferable to the pressure type of filter on account of the excessive operating cost of the latter. Filters of this type are employed by the Anaconda Copper Mining Company, the Inspiration Copper Company, the Timber Butte Milling Company, the Federal Mining and Smelting Company, and other large operators.

In smelting flotation concentrates for the recovery of the values therein, the ordinary practice is adhered to, dependent on the nature of the values—zinc, copper, lead, etc. The best practice recommends drying the concentrate before charging into a reverberatory or other furnace: *i. e.*, it is best to charge a hot calcine. If it is desired to reduce the sulphur content, calcines can be made in the ordinary McDougal or Wedge multiple-hearth furnaces.

RESUME.

Generally speaking, the mechanically- or air-agitated machines require fine material for successful performance: *i. e.*, 60-mesh or finer. In other words, most of the flotation processes are pre-eminently suited to the recovery of slimes. It would seem as though the flotation process should be used as an accessory unit in wet concentration, as an all-sliming plant, with few exceptions, is not an economic possibility in this country. The matter of rougher and cleaner cells is strictly a local consideration and must be determined separately for each individual plant. Two cogent factors enter into the solution of this problem: to wit, richness or leanness of the slime feed and proximity or remoteness from smelters. The dual, *clean and re-clean* method, was tried at Anaconda and finally abandoned in favor of the single cleaning method.

In the Callow¹⁷ process the pulp density may vary from 2.5 to 1 on a strictly sand feed up to 7 to 1 on a slimy feed. The particular density of feed is not a matter of such vital importance as is the necessity of a uniform density of pulp supply. In this process the quantity of oil used increases in proportion to the increased volume of pulp, and is independent of the solid content. Hence there is a dictum which says that the pulp should be run as thick as possible so long as other conditions operate satisfactorily. The advantages of

the pneumatic process are: greater recoveries, less oil, greater simplicity of operation, and less skill required to operate. It is known that a pneumatic froth is much more ephemeral than that made in mechanically-agitated machines, and this is an advantage in handling the resulting concentrates.

Universities teaching mining and allied subjects, particularly some of the state institutions in the West, having experimental research bureaus in connection, have taken up the matter of flotation research, as well as the determination of the amenability of ores and mill products, the subject of flotation oils, and other things relative to this process. The present and recently-formed co-operative plan of work among the United States Bureau of Mines, the State Department of Chemical Research of the Kansas State University, and the Mine Experiment Station of the Missouri School of Mines should have considerable bearing on the ultimate solution of some of the present flotation problems. The work at the Kansas Bureau¹⁸ and elsewhere has determined the amenability of the slimes of the Joplin district to flotation, and great savings could be effected were flotation plants installed in that district. The yearly loss in slimes in the Joplin lead-zinc area approximates \$11,000,000, which could be saved were flotation plants installed, thus contributing to the resources of the country.

Broadly, flotation has now reached a stage so as to find widespread commercial application. It is a noteworthy fact in the history of milling that such an apparently simple process should have such a ramified development in such a short time. There can be no question that flotation in due time will be a necessary adjunct in all the mills in the mining industry. Already the process has added greatly to the world's wealth. From its inception to date it has produced about \$20,000,000 in silver, \$1,700,000 in copper, \$612,000,000 in spelter, and \$19,800,000 in lead.

The complete reports from Michigan copper mines received by the United States Geological Survey show the production to be the largest in the history of the industry. The total refined copper produced amounted to 238,956,410 pounds according to B. S. Butler, as compared with 158,009,748 pounds in 1914 and with 231,112,228 pounds in 1912, the record production previous to 1915. At an average price of 17.5 cents per pound the copper output of Michigan had a value of about \$41,800,000 for 1915. The copper mines produced 585,933 ounces of silver in 1915, valued at \$297,068. There was mined and milled in the Lake Superior district 12,334,699 tons of ore-producing concentrates containing 265,283,378 pounds of copper, or a recovery of slightly above 1 per cent of copper from the ore. A portion of the concentrates produced was not smelted in 1915.

¹⁷Bull. A. I. M. E., Dec., 1915, p. 2321

¹⁸Metallurgical and Chemical Engineering, Nov. 15, 1915, p. 847.

THE NITRATION OF TOLUENE.*

By E. J. HOFFMAN.

Trinitrotoluene, the powerful explosive that is being used in enormous quantities in the war in Europe and is used in smaller quantities in the manufacture of detonators for use in ordinary blasting, is made from toluene, which is obtained as a by-product from the manufacture of illuminating gas and is also obtained by "cracking" petroleum, the process of manufacture being one of nitration. Various methods of nitrating toluene are in successful use but the published data regarding them are incomplete. In the course of an investigation at the explosives chemical laboratory of the Bureau of Mines, at Pittsburgh, it became necessary to work out the conditions under which the best yield of trinitrotoluene could be obtained from a sample of toluene under examination, and the method has been developed which, it is believed, can be satisfactorily applied on a commercial scale to the nitration of any toluene of approximately the same purity as that used. This toluene had a specific gravity of 0.8659 at 20/4. Fractionated with the use of a Hempel still head, 88.40 per cent distilled between 109.4 C. and 110.1°, and approximately 97 per cent between 108.4 C. and 110.1° C. Freezing tests made below zero and as low as -91 C. (uncorrected) indicated that the impurities did not exceed 1 per cent.

The method probably most commonly used in the industries for the manufacture of trinitrotoluene involves three separate operations: (a) the preparation of mononitrotoluene, (b) the conversion of mononitrotoluene into dinitrotoluene, (c) the further nitration of dinitrotoluene into trinitrotoluene. In addition to any other economical advantages this method may possess, it would be the obvious method where it is desired to utilize a part of the mononitrotoluene and dinitrotoluene products for purposes other than the preparation of trinitrotoluene. But where the sole object is the preparation of trinitrotoluene and no regard is had to intermediate products except insofar as these may affect the character and quantity of the final product, it would appear desirable to accomplish the nitration in not more than two operations. For the especial reason that it avoids the actual separation of the dinitrotoluene in the second stage of the nitration, the following procedure was selected as most satisfactory for development: (1) the preparation of mononitrotoluene from toluene, (2) the further nitration of mononitrotoluene to trinitrotoluene.

THE PREPARATION OF MONONITROTOLUENE.

The best results were obtained in this stage of the nitration by the use of a mixture of one part by weight of nitric acid of specific gravity 1.42 and two parts of sulphuric acid of specific gravity 1.84, the nitric acid used being 50 per cent in excess of that required theo-

retically for the conversion of the given weight of toluene into mononitrotoluene. The nitration was accomplished at a temperature of approximately 10 to 30° C. Either the toluene was added slowly, with constant stirring, to the mixed acid, or the reverse procedure of adding the acid to the toluene was followed. Examination of the respective products showed that the former procedure yields a mixture of approximately 60 per cent mononitrotoluene and 40 per cent dinitrotoluene, while by the later procedure very little dinitrotoluene was formed. By the former procedure the formation of any considerable proportion of dinitrotoluene could be avoided by the use of only a small excess of nitric acid, but in that case some of the toluene would escape nitration, and other difficulties would be introduced, such as of maintaining the progress of the reaction at a temperature of 30° and the formation of dark reaction mixtures, that often render impossible the separation of the mononitrotoluene from the spent acid by gravity. On the other hand the use of an excess of nitric acid greater than 50 per cent is to be avoided as it leads to the formation of a still greater proportion of dinitrotoluene which may separate out in the solid condition.

However, the formation of as much as 40 per cent of dinitrotoluene with the mononitrotoluene was not found to be objectionable, as the total product was to be further nitrated to trinitrotoluene, and for the reason that the temperature could be much more easily controlled, the procedure of adding the toluene to the mixed acid was generally followed. While nitration at a maximum of 30° was generally adhered to, the experiments did not show that the yield or character of the product was seriously affected by allowing the temperature at times to rise as high as 50°.

When the nitration was accomplished by adding the toluene to the mixed acids, the crude mononitrotoluene product, separated by gravity from the spent acids but not purified, was almost invariably 80 to 83 grams.

PREPARATION OF TRINITROTOLUENE FROM MONONITROTOLUENE.

In the main these experiments are included in three series.

Series 1—In this series of experiments the crude mononitrotoluene was dissolved in 100 per cent sulphuric acid and nitrated with a mixture of equal parts of 100 per cent sulphuric acid and nitric acid of specific gravity 1.5.

Series 2—The crude mononitrotoluene was dissolved in sulphuric acid of specific gravity 1.84 and nitrated with a mixture of equal parts of 100 per cent sulphuric acid and nitric acid of specific gravity 1.5.

In the experiments of Series 1 and 2, varying proportions of sulphuric and nitric acids were employed, as well as varying amounts of nitric acid in excess of that required theoretically to convert the mononitrotoluene into trinitrotoluene. The yield and quality of the resultant trinitrotoluene product were generally inferior. This appeared to be due, in Series 1, to the

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fact that in the initial stage of the nitration the acids were too concentrated, while, in Series 2, the second stage of nitration, dinitrotoluene to trinitrotoluene, was necessarily effected with acids that had become somewhat too dilute before the completion of the operation.

Series 3—In this series of experiments the difficulties encountered in Series 1 and 2 with respect to acid concentration were overcome by the simple expedient of performing the nitration first with weaker acids, then, after decreasing the water content of the resultant mixture by the addition of fuming sulphuric acid, completing the nitration with stronger acids. The temperature of nitration was found to be a factor of great importance. The best yields and the highest grade of product were obtained in those experiments in which the temperature was not allowed to exceed 117° .

The results obtained in the investigation lead to the conclusion that the following procedure will give the best results in the preparation of trinitrotoluene:

Preparation of Mononitrotoluene.—The acid used in the first stage of the nitration of the toluene is a mixture of two parts by weight of sulphuric acid of specific gravity 1.84 and one part of nitric acid of specific gravity 1.42, the weight of nitric acid taken being 50 per cent in excess of that required theoretically for the conversion of all the toluene into mononitrotoluene. For 50 grams of toluene, 73.38 grams of nitric acid are used.

To the mixed acid, cooled to 20° or lower, contained in the nitrating vessel provided with apparatus for cooling and stirring, the toluene is added gradually with constant stirring, the rate of introducing the toluene and the cooling of the reacting mixture being so regulated that the temperature does not exceed 30° . When approximately 70 per cent of the toluene has been added, the nitration becomes much slower and very little cooling of the mixture is required. When the total amount of the toluene has been introduced and the temperature ceases to rise, the cold water surrounding the nitrating vessel is allowed to run out, while the operation is continued about one-half hour longer. After standing, preferably over night, the spent acids are removed by gravity from the supernatant crude mononitrotoluene which consists of a mixture of mononitrotoluenes and dinitrotoluenes.

Preparation of Trinitrotoluene From Mononitrotoluene.—A. The mixed acid used in the first step in the conversion of the crude mononitrotoluene into trinitrotoluene consists of equal weights of sulphuric acid of specific gravity 1.84 and nitric acid of specific gravity 1.5, the nitric acid content being 50 per cent in excess of that required theoretically to convert the calculated yield of mononitrotoluene into dinitrotoluene. For the product derived from 50 grams of toluene, 54.58 grams of nitric acid are taken.

The crude mononitrotoluene is dissolved in sulphuric acid (sp. gr. 1.84) equal in weight to the

mixed acid and heated to 50° . The mixed acid is added gradually, with constant stirring, for a period of at least one hour, and during this time the temperature should not exceed 100° . After all the acid has been introduced, the mixture is heated for two hours at a temperature of 90 to 100° .

B. At this point the acids in the nitrating vessel, cooled to about 90° , are concentrated by the addition of 15 per cent oleum equal in weight to that of the mixed acid to be used in completing the nitration. If the oleum is added slowly very little rise in temperature occurs.

The mixed acid next used consists of equal weights of nitric acid (sp. gr. 1.5) and 15 per cent oleum, the nitric acid taken being double that required theoretically to convert the above nitration products calculated as dinitrotoluene into trinitrotoluene. On the basis of 50 grams of toluene, 72.78 grams of nitric acid are used.

The mixed acid is added gradually, with continued stirring, while the temperature is allowed to rise up to, but not above, 115° . When approximately 75 per cent of the acid has been introduced heating is required to maintain the temperature above 100° . A minimum time of two hours should be allowed for the introduction of the acids. When the addition of acid has been completed the heating is continued for two hours longer, maintaining a temperature between the limits of 90° and 117° , but not exceeding the latter temperature.

Upon the completion of the nitration the reaction mixture is allowed to cool in a vessel adapted to the subsequent removal of the spent acid. After standing at least 18 hours the crude trinitrotoluene will have separated as a solid cake and suspended crystals. After draining off the underlying spent acid the crude product is crushed, washed first with cold water, and then several times in the molten condition with hot water until free from acid, after which it is dried and tested. If a higher degree of purity is required this is obtained by recrystallization from a mixture of 9 parts by volume of 95 per cent alcohol and 1 part of benzene or by simply washing well with the cold alcohol-benzene mixture.

The spent acid contains in solution additional trinitrotoluene as well as lower nitration products which may be recovered by precipitation in water, but in practice the spent acid would be used over again after renewal by the addition of fresh acids. By the procedure outlined above a product can be obtained which when washed well with water amounts to approximately 75 per cent of theory and melts at 78 to 80° . From the spent acid an additional product can be obtained equal to approximately 8.5 per cent of theory, but which melts at 69 to 75° . After washing with the alcohol-benzene mixture the yields of trinitrotoluene become approximately 69 per cent, melting point 79 to 81° and 7.5 per cent, melting point 78 to 81° .

THE RENNERFELT ELECTRIC ARC FURNACE.*

By C. H. VOM BAUR.

The Stassano furnace was the forerunner of the Rennerfelt. The former started with a radiating arc, playing almost horizontally over the bath, whereas the latter furnace forces the naturally large arc flame violently down on the charge and away from the roof by employing a different method of electrode arrangement. Polyphase current of any frequency and voltage is used.

The advantage of a solid bottom has long been recognized, and the extensive use (33 in operation and 20 building) which this furnace has been put to in less than four years, is largely due to this feature in conjunction with the first-mentioned characteristic.

The Rennerfelt furnace idea is shown diagrammatically by Fig. 1.

The almost universally used 3-phase current is shown entering the transformers and is changed by means of Scott connection to 2-phase 3-wire system. The middle or combined conductor carries about 40 per cent more current in the vertical than in either of the side electrodes, and this forces the entire large radiating arc, by the resolution of forces and electromagnetic action, down on the bath. This form of arc has hitherto been unknown in electric furnaces. The horizontal electrodes are about 15 ins. (38 cm.) above the bath or slag, in some of the larger size furnaces, and the operating distance from tip to tip of the horizontal electrodes is usually from 18 to 22 ins. (45 to 55 cm.) or more. These dimensions give an idea of the size of the flame, which, striking the bath, mushrooms to the sides and ends of the furnace. The heat reaching the roof is consequently very indirect, thus favoring low roof-maintenance costs. These low roof-refractory costs have often proven themselves in practice; for instance, when melting cold steel scrap and making tool steel quality, heats taking 5 to 6 hours in a low-power furnace, at about 150 kw. per ton capacity of the furnace, the roof has lasted 192 heats with a 9 in. (23 cm.) brick. With faster melting and the 12 in. (30 cm.) brick, more heats could be expected per roof.

The furnace is built in different sizes. The first 30 furnaces were three tons and under capacity. Since then, a 4-ton has been placed in operation and second is expected to follow shortly. Eight-ton furnaces are building, while 12-ton and larger furnaces are being contemplated. Rennerfelt believes that with the multiple arc system, as years ago proposed in principle by Stassano, electric furnaces of 40, 50 and even 75 tons capacity can be made, and run to give satisfaction. A 40-ton furnace for instance would have four sets of electrodes of three each, the side electrodes 6 ins. (15

cm.) and the top 7 ins. (18 cm.) diameter, the furnace taking 4,800 kw. at the terminals. The inside diameter would be about 7½ ft. (230 cm.) and the hearth proper about 14 ft. (420 cm.) long.

On account of the peculiar characteristic of the Rennerfelt arc, it is very steady with hand regulation, and the furnace operation is electrically simplified to a marked degree, by avoiding all automatic electrode regulation, although motors with push-button control are contemplated. As only 4 or 6 lbs. (1.8 to 2.7 kg.) of Acheson graphite are burned away per ton of cold steel scrap or pig melted and treated, it is evident that the electrode regulation with such a steady arc, made between three points of stability, that is, the tips of three electrodes, is a minimum, and this has been proved in practice. The electrodes oftentimes do not have to be adjusted for a half hour, and still the power

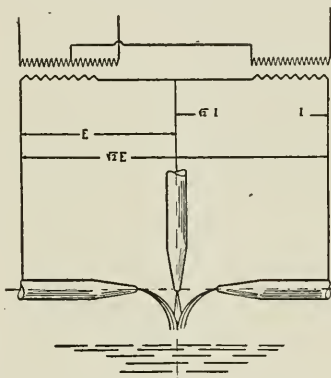


Fig 1—Electrodes and Connections.

consumption is about as steady during these periods as with an induction furnace. Light metal scrap or turnings can be heaped in the furnace with the electrodes touching the charge, and yet before many minutes the free-burning arc between the electrode tips has established itself.

All but three or four of these furnaces are operating, or contemplate doing so, with basic bottoms. Only a few operate with acid bottom, and these in tool steel works where the highest class of raw material is available at reasonable prices. The bottoms of these furnaces last as long as similar solid bottoms of open-hearth furnaces. The sides burn away a little faster and wear away also, due to the slag action, and the roof goes faster than the sides, but lasts as long as previously mentioned.

The wear of the electrodes seems to depend on three things: first, the density of the current; second, the circular area and length exposed inside the furnace; and third, the amount of air leaking into the furnace. The latter cause seems to have the most deleterious effect and hence doors are fewer now than formerly. Up to the 3-ton size there is only one door and that

*Paper presented at the 29th meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

over the spout, all other furnaces have but two doors and these are much tighter. The clearance of the cooling boxes is also made less. Only $\frac{1}{8}$ -in. (3 mm.) clearance is allowed, which is just enough room to compensate for the slight irregularity in the manufacture of what are ordinarily perfectly round electrodes.

The electrical conditions are most satisfactory, as evidenced by the opinions of Central Station managers. On account of the high power factor at 50 to 60 cycles, it being 90 to 97 per cent, the phase displacement is almost entirely avoided, and the phases are almost perfectly balanced.

The so-called efficiency of electric furnaces depends, as has been broadly discussed by Hering and others, on the rate at which the heat is forced into the furnace, besides upon good insulation, proper painting, etc. The main point of these is the rate at which the power is consumed. Three or four years ago, 200 kw. was considered ample for a 1-ton furnace; now 350 to 375 for this size is common practice. Consequently the melting time has decreased and the kw. hours per ton are less, the cost of the steel in the ladle is less, and the output is correspondingly increased. The practical limit to this high-powering of furnaces is the power of the refractories to withstand the higher heat for sustained periods, the refractories are also subjected to greater differences of temperature between heats, specially with those furnaces where the electric current cannot be maintained while there is no charge in the furnace.

With low-powered Rennerfelt furnaces the power consumption when treating various metals has been as follows:

	K.W.H. per metric ton.
Melting red brass	168
Melting pure copper	197
Melting white iron	290
Melting gray iron	325
Melting 80% ferro-manganese	441
Melting steel scrap, not ready to pour	455
Melting and "killing" steel scrap on an acid bottom, about	600
Melting and refining steel scrap on a basic bottom, about	700
Melting 80% ferro-manganese and holding, tapping and charging	741
Making 67% ferro-tungsten, small scale	5,730

The characteristic features of the furnace may be summed up as follows:

(1) The heat is generated with an arc with the absence of exceedingly hard strains on the power supply.

(2) On account of the steady power and on account of the large flame widely diffused the heat is communicated to the charge quicker than with arc of the thin-penciled type, made between the tips of the electrode and the bath.

(3) A large flame or a series of them sweeps all over the major portion of the charge in the center of the furnace, or at regular distances along the major axis of the furnace, and is directed and violently deflected downwards.

(4) The heat being thrown downward in this way and being a radiating arc of large volume, these are features favoring higher efficiency, other things being

equal, and the roof therefore has a long and satisfactory life.

(5) There is only one small hole in the short-radius roof for each set of electrodes, both of these features making for strength and lower maintenance cost.

(6) The hearth is more easily surveyed and accessible, during operation, than in arc furnaces having electrodes only 2 or 3 inches (5 to 8 cm.) above the slag.

(7) With larger furnaces multiple arcs are used, this method starting in with the 6-ton furnace. The heat distribution is markedly better than with arc furnaces of equal size, using the metal to conduct the current in one form or another.

(8) The heat is applied more directly, although the arc is not.

(9) The heat gradient in an electric arc is greater if it takes place in the widely-spread-out heating zone rather than in a narrow space.

(10) The radiating arc is a much more rapid way of transmitting heat than the slow heat of conduction of other arcs.

(11) There is no water-cooling below the bath, which consequently avoids danger of explosions from this source.

(12) The voltage at the arc is from 75 to 100, depending on the furnace size, and these potentials are harmless if a shock is experienced.

(13) The amperes per electrode in large furnaces is small, namely, only 5,400 and 7,700 in a 3,600 kw. furnace, whereas with other 3-phase and 3-electrode furnaces this would approach, at 80 per cent power factor at 110 volts, 23,600 amperes. This higher amount of current brings with it difficulties of the skin effect, because these larger current have to be brought to single electrodes.

(14) The hearth bottom is burned in by the arc without the use of coke or other material.

(15) The electric current can be kept on the furnace during tapping and charging, thus keeping the furnace at a more uniform temperature, with its consequent advantages of keeping the refractories from checking. The furnace thus does not cool down and a saving of 10 to 20 minutes in time can be made on this account per heat, this being the usual charging time; whereas most other electric arc furnaces have the current shut off during the charging period because it is unavoidable.

The production of coal in Michigan in 1915 was 1,156,138 short tons, valued at \$2,372,797; in 1914 it was 1,283,030 tons, valued at \$2,559,786. The average value per ton in 1915, \$2.05, was 6 cents greater than in 1914 and exceeds any record for the state in recent years. Coal consumption in Michigan is increasing every year, but coal from other states supplies a large part of this market, and the decrease in output in the Michigan field last year, which amounted to 126,892 tons, is attributed by the United States Geological Survey to this cause.

A POSSIBLE SUBSTITUTE FOR THE IMPORTED VANDYKE OR CASSEL BROWNS FROM DEPOSITS IN THE UNITED STATES.*

Owing to the fact that the imported Vandyke or Cassel browns (soluble and insoluble) are now obtainable with great difficulty and at a price nearly five times normal, it is deemed advisable to report what has been observed as to available browns of this class occurring in this country.

A large amount of these browns is imported in the insoluble form and is worked up in this country by extracting the raw material with sodium carbonate solution. There appear to be no available statistics as to the amount of this material actually used, but it is known to be used in large quantities especially by the paper trade. At the present time there appears to be little Vandyke or Cassel brown on the market, although the quoted price is somewhere around 7½ cents per pound. In normal times the price is very much less and it appears to remain around 1½ cent per pound.

Of the soluble browns there is seemingly between 1,000 and 2,000 tons used annually in this country in normal times, largely for coloring paper, the material being readily fixed thereon by the addition of certain electrolytes or by slightly acidifying the solutions.

Samples of the dry material have been sent to two experts in the color trade, both of whom have used the imported material, and there seems to be little if any difference between the material described below and that procured from foreign countries.

It would therefore appear that an investigation of these deposits by those interested in paper colors would probably lead to the development of a large domestic supply.

There is a deposit of water-soluble brown organic material, lignitic in character, situated 6 miles east of Hanna, Wyoming, possessing in general the following characteristics:

(1) It is sticky, viscous, and nearly solid, dissolving readily in water to a dark-brown liquid, which becomes yellowish in dilute solution. It is insoluble in alcohol (absolute), benzole, xylol, chloroform, benzine, or other common organic solvents. The solution in water is seemingly colloidal. The residue insoluble in water consists of a clayey silt or sand and finely divided organic matter, chiefly plant remains.

(2) The color may be precipitated from solution on paper by alum, barium chloride, or other metallic salts in the same manner as the brown obtained from the imported material by solution in dilute alkali. The color of the domestic material (soluble) is seemingly fully as good as that of the imported brown, and possesses the advantage that it is already in the solu-

ble form, whereas with the imported brown dilute alkali must be employed to effect solution. Dilute mineral acids precipitate the color as with the imported brown.

(3) The dried material grinds well in oil; the color, however, is not so good as that of the imported browns, although the color is developed at once by the presence of water. It is thought that the color in oil may be improved simply by not carrying the air-drying to completeness, or by emulsifying with a small amount of water. The sample tested was thoroughly air-dried but the indications are that the substance will carry considerable moisture and still grind well in oil.

(4) The liquid obtained by leaching contains finely divided clay in varying amounts in suspension which it is almost impossible to remove completely, but it is probable that this clay would itself act successfully as a filler where the color is applied to paper—its chief use.

The following results of a proximate analysis of a sample from the Hanna deposit give a further idea of its characteristics:

PROXIMATE ANALYSIS OF WATER-SOLUBLE BROWN ORGANIC MATERIAL FROM DEPOSIT NEAR HANNA, WYOMING.

Item.	Percent.
Loss in air-drying	56.85
Moisture in air-dried sample (105° C.).....	8.95
Total water soluble	48.29
Ash	42.50
Soluble alkaline salts (weighed as chlorides).....	4.24
Otherwise stated:	
Organic water soluble	44.05
Ash	42.50
Organic insoluble	4.50
Alkali metals, mostly sodium:	
Analysis of the water soluble: (ash free)	
Carbon	56.51
Hydrogen	5.74
Nitrogen	1.81
Oxygen	35.96
Analysis of color precipitated by adding dil. HCl to the solution, the precipitate having been thoroughly washed with HF1 and HCl to remove mineral matter:	
Carbon	61.84
Hydrogen	3.36
Oxygen plus nitrogen	33.30
Ash	1.50
Analysis of precipitate produced by the addition of BaCl:	
Carbon	45.80
Hydrogen	3.45
Barium	22.65
Oxygen plus nitrogen.....	28.10

Little is known as to the number and nature of the bodies contained in this substance, but the indications are that it is chemically very complex.

OTHER DEPOSITS.

Another deposit of lignitic material similar to that obtained from Wyoming is described at length by Mr. William Foster (Econ. Geol., vol. 8, No. 4, June, 1913). He says, "The deposit is located in the north-western part of New Mexico, about 15 miles north-west of Putnam, and is marked on the old maps, Pueblo Bonita. It is on a high plateau—4,000 to 5,000 feet—adjacent to the Navajo Indian reservation."

The deposit is near the surface—about 4 feet—and is more than 10 feet thick, extending over considerable territory. The properties of this substance are very similar to those of the Wyoming deposit, and

*From notes of the late Prof. Chas. A. Davis, past expert of the Bureau of Mines, who was making an extensive investigation of these substances. Published by permission of the Director of the Bureau of Mines.

the analysis given by Mr. Foster agrees very closely with that given above.

A like deposit is found also in Montana about 8 miles south of Box Elder, a station on the Great Northern Railroad, between Great Falls and Havre. The outcrop from which the sample was taken is in a coulee; the thickness of the vein is 1 to 3 feet, the width being about 10 feet. The vein is described as being "more or less exposed."

Other deposits have been investigated, but those described above seem to be the most promising as sources of the commercial earth browns.

THE AMERICAN CHEMIST AND THE WAR'S PROBLEMS.*

By JAMES R. WITHEROW.

A volume could be written upon this subject if one possessed the power to assemble the material. The new problems which have arisen; the old ones which have become acute because of changed conditions; the splendid way in which the problems have been met where they were a matter of invention or skill; the new methods and processes which have sprung up as though born full-grown; the many old ones which have been improved, altered and utilized in new connections; the way in which the chemists of the country have risen to emergencies which have compelled them to manufacture products in whose manufacture they had had no prior experience—all these would easily fill entire chapters in such a volume. Even so, no earthly progress, achievement or consideration can lift the pall which settles over us when we permit our minds to dwell upon the spectacle of this war. And whose mind can be diverted from it for any length of time? He must indeed exist far below the kindling point who does not resent and despise with all his soul the philosophy and ideals which made it possible.

It would be out of place, therefore, to consider our subject from the point of view of achievement, or felicitation, on any alleged good which has come to the science of chemistry because of the war. Surely no one would want progress at such a cost to his fellow man. We approach the subject rather in a spirit of thankfulness that we have been enabled to save something out of the wreck, and that our experience had prepared us in advance so that we have been enabled to prevent the collateral business and economic tragedies of the war from spreading universally. It is not in any spirit of gladness, therefore, at the evil providence which has fallen upon our European neighbors, that we recognize that this war has exalted the importance of chemistry in the minds of those who had not much opportunity hitherto to appreciate its value, nor is it with any jubilation that we take pleas-

ure as chemists in meeting our new problems and emergencies arising from the war.

The satisfaction to many industrial chemists in the last two years of being able to contribute to the solution of these problems and of being conscious of the salvation of many businesses from financial ruin through the exercise of their chemical experience, has seldom been so widely distributed as it now is. What an inspiration it would be to read, spread out upon the pages of such a book as we have mentioned, the chemical successes, big and little, of the past two years. It is not likely that many of them will be known for a while because of the fact that business caution forbids their publicity in many cases, and that the vigorous campaign of destruction of equipment and diversion of supplies in order to hamper export from this country, makes silence a necessity in self-defense.

The problems of the war are of two kinds, those due to changed conditions, and those arising from supplying munitions at high speed. Among the former are changes in raw materials made necessary by the failure of imports or by unusual consumption of raw material in other channels, such as for products not heretofore manufactured in this country, to the extent made necessary under present war conditions. These changed circumstances were also due in part to new demands for materials and products, which have arisen in the complete re-arrangement of things that has come about in many circles since the war began. The other war problems which have arisen, those directly connected with munitions supply, are frequently of a difficult nature. All these various problems, however, have been met in practically every case with a degree of success that has surprised even ourselves.

Naturally one of the first serious effects of the war on American industries was the stagnation produced by the enforced cessation of exports in various lines. Such things as rosin, turpentine, petroleum products, acetate of lime and methyl alcohol were seriously affected for a varying length of time. Then the demand for munitions, for instance, became the wood distillation industry's salvation and with great celerity, acetone plants were attached to many of the works of this industry and the high prices which its products command have brought unprecedented prosperity and have correspondingly hampered progressive improvements. Production, not efficiency, is at present the slogan for this and many other industries. Setbacks of the nature cited usually take time for readjustment and frequently the chemist is a material factor therein. The producer himself is often compelled to add the next manufacturing step to his own operations. Where the new demands were ample, these attempts have succeeded and the war's conclusion will find an increased tendency to manufacture at the source.

The setbacks to industry arising from the disturbance in exports, while they were important financially, were minor matters compared with those arising from such changed conditions as failure of raw materials

*An address presented Dec. 30, 1915, before Section C of the American Association for the Advancement of Science, Columbus, Ohio.

or their curtailment by absorption in new or abnormally expanded industries. It is here that the chemist is needed most and it is here that he has been of immeasurable service, and has met the problems that have arisen in wonderful style. He was seriously hampered at first by the uncertainty as to the facts. The fundamental thing in every industry is the market. At first much damage was wrought and delay produced by false reports as to stocks on hand and supply, particularly, of imports. Much withholding of goods for higher prices was practiced and even yet the pirates of commerce seek ways and means of evading contracts, even on deliveries of goods which they were receiving without cessation, so as to avail themselves of the inflated market prices. Some clever work by consumers trapped at least some of these unscrupulous brokers and sellers. All manner of fictitious prices were demanded of those unfamiliar with the facts.

As soon as the true status of demand and supply became reasonably certain, many changes were effected which will give gradual and probably ultimate relief. On every hand we see chemical activity without end. Products like synthetic phenol and barium salts, not made in this country before the war, are now made in large amount. Great expansion in production has taken place in the case of such materials as benzol, toluol, aniline products, naphthalene, carbon tetrachloride, acids, alkalis, chlorates, bichromates, and even oxalic acid. With all of these we were largely or in part dependent on imports, but have almost ceased to be so since the war began. Now, fertilizer plants erect their own sulfuric acid works and insecticide makers their own arsenic plants, textile mills make their own bleach. Numbers of manufacturers are replacing potash compounds by sodium compounds and to my own surprise at least, often with great improvement in results. Professor Watts has told you how the ceramist is making this country less and less dependent upon imports in that field by scientific purification and utilization of domestic clays. Manufacturers of numerous miscellaneous chemicals and pharmaceutical preparations proceed to refine and produce their own crude raw materials and intermediates. The dye famine—for it is real in certain quarters—stirs up corporations with capital of hundreds of millions to enter the field. One of these new companies has installed half a million dollars' worth of machinery in the last few weeks. Indigo and other dyes are being made in nearly half-ton batches which will soon expand to a several-ton size. Where formerly was the most peaceful of occupations, even fertilizer manufacture, every effort now goes to the making of munitions. New plants spring up at the beck and call of new conditions such as the world has never seen. Think of a battery of 100 nitric acid stills each charging 4,000 lbs. of sodium nitrate three times a day! Think of The sulphuric acid required and the nitric acid produced! Think of the fact that this one of a

number such (the largest nitric acid plant in the world, it is said) is a plant which a year ago did not exist except in the mind and plans of a group of chemical engineers. How little are we able to comprehend the reality of producing 1,000,000 lbs. per day of guncotton where a year ago was merely pine woods. What does it mean with reference to design of plant, erection and operation to anyone who has not managed chemical engineering operations, to recount the engineering operations involved in this enormous production of guncotton in a single plant?

Work that is conducted in ten to fifteen parallel procedures or "cotton-lines," which with their accompanying accessories include cleaning and alkali digestion of the cotton; bleaching with chloride of lime; manufacture of sulphuric acid for the production of nitric acid and "mixed acid"; nitration of the cotton in 30-lb. batches; the hazardous wringing and hasty submerging of the cotton in water, to avoid the consequences of heating by too slow dilution of the strong acid held sponge-like by the cotton; the conveying of this material in the "cotton-line" to the washers where the remaining acid in the tube-shaped cotton fibers is removed; and finally the removal from the water as wet or damp guncotton, the commercial product of many plants. This end-product, of course, is but the beginning of raw material for the various nitrocelluloses, smokeless powders and other high explosives. Yet this scale of operations is not going on in just one plant of this kind or even in this one industry. This is a sample of what is happening every day and is the American chemical engineers' answer to the question, "How are you meeting the war's problems?"

At some of these things we are permitted to take at least a peep. No one man can know all of even such gross developments, and practically every chemist we meet has his enthusiastic story of the progress of his own and familiar fields. We all do know, however, that if this is the character of the outward developments, there must be legions of quiet research and other experimental attacks on the new problems, and literally hundreds of solutions being worked out for minor problems in factory and plant, not to speak of the vast amount of work in other departments of chemistry made necessary by all these things. Then, too, there is the ever-verdant crop of interesting suggestions, revolutionary changes and inventions throughout the list of the chemical industries. In fact, they are doubly numerous and aggressive under the stimulation of such a time as this. It is never wise to predict their success or failure in many cases until years even have elapsed. It is true that a large number of these new things *never* make good. It is equally true that some of them *will* make good and that all of them indicate progress, for they are strivings, and progress comes by striving.

It is equally true also that many of the chemical expedients which are in successful use under war conditions will automatically be put aside when normal

conditions resume. It is fundamental industrial chemical intelligence that a procedure which is ridiculous under some conditions may be a godsend under others. We do not expect every change installed to be really normal progress, for it will not be so in the ordinary sense at least. On the other hand, it would be wrong also to say that the mushroom plants producing munitions are not signs of progress. They unquestionably are not such signs in so far as they are temporary. They do not measure true expansion in their respective fields. He would be a novice or singularly blind, however, who did not see that the construction of such plants on the un-dreamed-of scale I have already mentioned, not to speak of the new materials and procedures which have been incorporated in many of them, makes for greatly enlarged experience in chemical engineering designing, construction and operation. It is easy to see the pressure these things are going to exert upon the future development of American chemical industries. The American chemist's experience is becoming greatly expanded and the significance of this is apparent when we consider that engineering progress is a function of demand and skill or experience in solving problems. The demand increment is ever expanding with the development of the country. In addition, the skill acquired in the production of munitions is a valuable potential asset for defense should such a necessity ever arise. Such preparedness is highly to be desired. Then, too, at the close of the war when the output of these plants is no longer needed for that purpose, their equipment and intelligence will be directed into whatever field promises most. Already some of these concerns are assured that some of their products will find a continuous demand after the manufacturing of munitions ceases, which will be some little time after actual hostilities are at an end. The field of dye production is already attracting some of them. Without doubt the industrial re-arrangements to follow the war will leave us much better situated in our ability to cope with the problems of chemical production. At any rate, powerful financial interests will attack these problems as they never have been attacked before. These interests will constitute another great force, which will be particularly effective after the war. When they seek new outlets for materials such as alcohol, benzol and acids, whose production they are greatly accelerating at the present, the gasoline and other problems will be greatly affected. These interests will be found after the war lined up behind the industrial chemists who have been struggling for years against all kinds of unfair competition and disreputable depreciation. Then again, any change in process, be it ever so timeworn or transient in its chemical nature, if it actually is put into successful operation under the then existing conditions, must of necessity push out the boundaries of experience to greater and greater distances and make us better able to meet the problems of the future. Chemical engineering is like any other division of en-

gineering, it grows by what it accomplishes. In this proof of ability to meet a transient emergency the American chemist is certainly reaping a hundredfold as a result of his unadvertised care in the meeting of his industrial problems of the years gone by. Individual cases of progress and development which I have mentioned, it is easily seen, are rarely of great importance in themselves. We have not been revolutionizing on a great scale nor have we been jumping at once into great, new, national industries, but we are rather directing the normal steady gait of our progressive industrial development, with a keener perception toward more complete self-containedness, and thorough industrial preparedness. Some of the industries mentioned which receive much public attention are of relatively little importance compared with many other items affected. The dyestuff shortage appears to annoy many, but the complaint is out of all proportion to the facts and the damage done, compared with that of other commodities. We import normally, for instance, \$9,000,000 in coal-tar dyes per annum, and if we should make them all ourselves—which we will only gradually approximate—we would increase our chemical manufactures only 2 per cent and our total manufactures 0.05 per cent.

Though we have made reasonable headway on our problems we are keenly aware that much remains to be done. We do not expect to set the market right in the dye or other matters, in a year or two. These developments take time and have always taken time. Neither should we deceive ourselves or the public with thinking because of what we are doing that we could turn out, without the most careful and detailed previous planning, adequate munitions for our own defense "in sixty days" to supply the "two million men who would spring to arms," as we so often hear would happen in that undesired emergency.

It would be interesting to discuss in detail some of the transient, as well as probably permanent, advances, where they happen to be a matter of personal knowledge, if it were wise to hand information to the assassins who lie in wait to hamper some of them, for military reasons. It might be well, therefore, to spend just a little time in emphasizing some general considerations which are connected with this subject.

There is little use in attempting to disguise the fact that the present war is a struggle between the chemical engineering genius of the Central Powers and that of the rest of the world. Quite irrespective of the war's origin, aims, ideals or political circumstances, these are the cohorts from which each side derives its power.

When we consider the strategic position of the Central Powers themselves, their capable education and training, their system of government, which, no matter what we may think of its selfish effect on the world as a whole, we must admit makes for more effective concentration upon its own governmental objectives—when we take into account all these things it must

often appear to us that the greatest outstanding feature of the past two years is the miracle of the Entente Powers' resistance to the terribly efficiently prepared onslaught of the Central Powers. This resistance is due, to an extremely large extent, to the efficiency of the chemists of the neutral and Entente nations. The chemists of the Entente Powers and of America have arisen to the emergency as no chemists have ever done before in the history of the world. Confronted at the beginning of the war by antagonists whose munitions industry for years had been developed for just such a contingency, these chemists have in less than two years built up a rival industry at least as strong. Plant after plant has sprung up of such perfection of design and operation that one wonders how the mind of man was capable of such engineering. Though the speed with which these new and unexpected problems have been solved may appear surprising, no one who is informed as to the progress and development of industrial chemistry in this country could have reason to doubt that American chemical engineers and industrial chemists would rise to any emergency which it was within human power to meet. They have already and will continue to live up to what we have a right to expect of them, in view of their past successes. We would be surprised if a similar degree of success did not crown the efforts of the chemists of the other countries, France, Britain, Italy, Germany, Austria and Russia; for it has never been the habit of American chemists to boastingly claim superiority because of any advantage, real or imaginary, with which they, like any group, are apt to be blessed for a greater or less period of time. We have always appreciated chemical contributions to progress from whatever source they have come and praised unstintingly the individual, wherever he may be, who has taken a distinct step forward, for we firmly believe this is an important help in advancing the progress of the science.

These general developments are naturally not a matter of public information, except when attention is called to them. The chemist works almost entirely beneath the surface of things, and only in a few spectacular cases is public attention drawn to his work. It is quite natural, therefore, that appreciation and praise of foreign chemical achievement and particularly our consistent praise of German achievement to our students by our university teachers of chemistry have been misunderstood, and have prepared a fertile field for foreign propagandas to establish a false impression of the superiority of certain groups of foreign chemists. We would scarcely object to a good-natured adulation of anyone's fatherland and its achievements. Such things always contain good and are stimulating to everyone, and it is a pleasure to hear them when free from arrogance, even when the adulation contains little that is new or even strictly true. When, however, this privilege is abused so that the point of superiority must be made by depreciating American efforts it has a vicious, positive result upon the minds

of the uninformed, and at times causes great financial loss to them.

If the shortcomings of American chemistry were frankly discussed and compared with foreign successes in a chemical publication, some help might be given to those who could derive benefit from it. When this is *not frankly* done, but simply issued as an incidental *depreciation* of American chemistry, particularly when discussing foreign chemical achievement, and still worse when in a non-chemical publication, the object can scarcely be rated as creditable.

If the myth of the overwhelming industrial chemical superiority of German chemists ever was really believed in that country, the military forces of the Central Powers at least must marvel at the way the supposedly inferior foreign industrial chemists have displayed such astounding ability and speed in meeting the problems of munitions production, particularly, too, in countries where governmental mobilization of industries was unknown before the war and, in America at least, still is unknown. At any rate it has become evident that lack of self-advertisement is no sign of lack of ability or activity, and that ability to handle science skillfully and powerfully is not confined to any one race or nation. We do not feel that there is much to be gained by confuting claims of the chemical superiority of foreign countries in this and other similar articles, for it is curious how this war has developed farsightedness to the extent that some *Americans* can see only the chemical developments abroad.

I hope I have made it clear that it is the abuse of a privilege against which I speak, and not against individuals, for we do not let narrow-minded attacks affect our regard for individual Germans any more than we allow our opinions on the history of the past two years to affect this regard for such individuals. Everyone of us know Germans who are the most whole-souled and kindly men—who we are grateful to know and who scorn to be guilty of, or take advantage of, chauvinism. Depreciations of American efforts will bury themselves, without any assistance from us, and I emphasize them here only to call the attention of teachers of chemistry to the fact that *we* owe protection to the business community and the public against such misrepresentation. We should never cease our appreciation of foreign chemists of whatever nation, but in addition it is our duty first to inform *ourselves* and then our students as to what our own chemists have done to solve our problems in this country. We have been able to blame our shirking this duty in the past upon the fact that it was easy to get information about foreign chemical achievement and no one seemed anxious to give publicity to American development. We, as teachers, have certainly done little to remedy this condition. The American Chemical Society, however, has spread the results of American efforts before us and made them accessible in its *Journal of Industrial and Engineering Chemistry* for the last two years, in the shape of a series of

addresses on the chemist's contributions to American industries. There are other addresses in these same volumes profoundly informing along these lines and this is particularly true of the Perkin Medal addresses each year in the same journal. In addition, Prof. S. P. Sadtler, in the *American Journal of Pharmacy*, for October, 1915 (an address before the National Exposition of Chemical Industries), in giving popular information along this line limits himself entirely to chemical industries *originated* as well as developed by the American chemist, and Edgar F. Smith's "History of Chemistry in America," but recently issued, should be read by every student of chemistry.

None of this work is in any sense a vainglorious adulation of the chemist as some superbeing, nor is it an attempt to compete in the questionable game of lauding one nationality above another. It is merely a matter of a belated form of education which our universities and chemists hitherto have largely denied to the American business man, and which he has a right to expect of them. The record is one for which we have good reason to be thankful and, as we teachers no longer have the excuse of ignorance about American progress, we are at fault, if the rising generation has not an appreciation of the progress of chemistry in America, commensurate with the high level of its development.

In conclusion then, let us take courage from the fact that though much damage has been done to us and our industries by the war, our efforts at salvage benefits us as experience, power and preparedness. We have seen that the chemists of America have met the war situation well and do not require defense at the hands of anyone. It becomes increasingly evident that business has been awakened to the value of chemistry as a source of power and wealth as business has never had occasion or opportunity to be hitherto. Let us hope also that not only the spectators but also all the combatants may learn, even if impelled by bitter war's experience, to appreciate the worth, each of the other, and that all nations are "made of one blood to dwell on the face of the earth."

An Argentine joint stock company with an authorized capital of \$125,000 has been organized under the name "Compañía Argentina de Materias Colorantes," with the object of producing dyes. The material to be employed is chiefly wood of the carob tree, treated in accordance with a new process discovered and patented by Dr. Juan A. Dominguez of Buenos Aires. The colors produced are khaki and fawn, and other colors obtained by combination. A factory has been erected at Santa Fe, according to the River Plate Review of March 24, and manufacture is to begin immediately, under the direction of the board of directors, whose president is Esteban Baron.

THE BLAST FURNACE AS A POTASH PRODUCER.*

By CHARLES CATLETT.†

It is remarkable that so little has been done in the way of saving by-products from the blast furnaces producing pig-iron. Such efforts as have been made have been mainly to utilize the heating values in the gases by burning them in hot blast stoves, under the boilers, and, more recently, in gas engines, thus insuring a surplus of power. The slag has been used as a basis of cement, and to a much larger extent as a substitute for crushed stone. In some furnaces small amounts of zinc oxide are deposited in the flues, or mouth of the furnace, as a hard crust, which, when it becomes an obstruction, is removed and a market is found for it. In one furnace I know of a small amount of metallic lead is regularly collected, and this lead carries good values in gold and silver.

But no serious consideration has hitherto been given to the much greater possibilities of value which exist in the form of substances which occurred in small quantities in the raw material, or which are formed in the process of reducing and smelting the ore, and which are carried out in the gases as dust or fume and thus permanently lost.

It is unfortunate that, either because attention has not been focused on it or because simple and satisfactory means for saving such material are supposed not to have been devised, comparatively few analyses and determinations are available showing the amount of these losses. But enough is in hand to give some idea of value, and data which the writer has collected and certain analyses which he has had run in his laboratory lead him to venture the opinion that the by-products which can be collected from the blast furnace gases are sufficient in value to profoundly affect the question of the manufacture of iron in certain sections and from certain materials. He presents these facts in this incomplete form in the hope that the suggestion may be some contribution to industrial preparedness, and may aid in the movement which seeks to produce all necessary things within our own borders, and that others may thereby be tempted to go into the matter in more detail.

Possibly the most important by-product in the light of present events is potash. In regard to this there is limited but interesting data.

Every investigation of a blast furnace problem goes back to Sir Lowthian Bell's monumental work on the chemical phenomena of iron smelting. In this he calls attention to the presence of potash in the burden, the source of which in that case he attributes almost entirely to the ash of the coke, and discusses the formation of potassium cyanide in the furnace and its influence on the smelting operations. He also reports determinations of potassium cyanide at various

*From the Manufacturers' Record.

†Staunton, Va.

levels in the furnace. Incidentally he gives figures, as the average of a number of determinations, showing the amount of potassium cyanide in the gases issuing from the furnace. *An approximate expression of these figures would be 6 tons of potassium cyanide for every 100 tons of iron produced.*

If we assume 80 percent recovery, which is easily possible, by passing the gases through an electric separator before going to the stoves and boilers, we would have 4.8 tons of potassium cyanide per 100 tons of iron produced.

But potassium cyanide is at present quoted at \$2,000 per ton, while the common cyanide on the market, which is mainly sodium cyanide, brings \$600 to \$700 a ton in large quantities. It is true that in normal times before the war the value of potassium cyanide in bulk was about one-fourth of this, or \$500 per ton; but \$24 per ton of iron in the form of by-products which may be saved is not bad, when the iron industry in the Birmingham district is booming on a sales price of \$15.50. And this does not take into consideration the sodium cyanide, the zinc and the lead, all of which in some furnaces are in considerable quantity.

A very proper criticism of these figures would be that they refer to a certain furnace and a certain series of operations.

But there is another way of making an approximate estimate. The potash driven off must be represented by the amount going into the furnace, less the amount lost in the slag.

The analyses showing potash in furnace slag which I have been able to find show very considerable variation, but a number show less than .4 percent. One recently examined in my laboratory shows .36 percent. Let us assume that the slag in a given furnace carries .4 percent potash (K_2O).

Pure limestones are usually low in potash, but a number are recorded carrying over .3 percent potash. Let us assume that the flux carries .3 percent potash.

A number of cokes show as much as .3 percent potash. We will assume that figure.

Iron ores are variable. The leaner, more silicious ores are apt to be highest in potash. There are few analyses published showing potash, but I find a number between 1.50 percent and 2 percent and one which shows over 2 percent. The most conspicuous examples in the South are what is known as the "Gray Ores" of eastern Alabama, which are in good state of development at Columbiana, Emahee and on the Heacock-Riser property near Talladega. These ores are quite low in phosphorus and carry about .4 manganese. They have been shown to work well in the furnaces and to make an excellent grade of iron. A number of analyses run very high in potash, but there is good reason to believe that they can be depended on to furnish about 1.50 percent of potash. While much of the ore is of higher grade, it will be assumed

for the purpose of this calculation that the ore carries 42 percent iron.

A rough calculation on a normal mixture would give:

Potash from 2½ tons ore	.035 tons
Potash from 1½ tons coke	.0048 tons
Potash from 1.2 tons limestone	.0036 tons

Potash going into furnace per ton iron	.0434 tons
Potash lost in slag per ton iron	.0060 tons

Potash driven off per ton of iron	.0374 tons
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The potassium would probably all be present as cyanide and would correspond to about the same as reported by Sir Lowthian Bell, viz., 6 tons potassium cyanide per 100 tons of iron produced.

The interesting thing is that the potash is apt to follow the silicious impurities, so that those furnaces which are at a disadvantage on account of what is spoken of as a low-grade material may by the utilization of the by-products produce iron cheaper than other furnaces which are at present blessed with the purest of raw material.

Of course the extreme figures of value are the product of unusual conditions, but figures for normal times are sufficiently startling, particularly when there is added the value of the zinc and lead and other substances which certainly occur in greater or less quantity.

Potassium cyanide is used to the extent of about a million and a quarter dollars annually; but its consumption would certainly be largely increased if the cost could be reduced so there would be no danger of overstocking the market. It is largely used in metallurgy for the recovery of gold, and is also the basis for the manufacture of Prussian blue. As it represents an instance of the fixation of atmospheric nitrogen, there is little doubt, if it could be produced cheaply enough, that it would be used as a source of nitrogenous compounds.

If the gas is not treated till it is burnt in the stoves and under the boilers, the cyanide would be destroyed and the potash would no doubt occur as the carbonate of sulphate. There is no limit to the demand for potash at a price. It is probable that large quantities could not be sold for more than \$300 per ton (based on pure K_2O), even though much higher prices are paid at present for it. Even on this basis the potash alone saved from such a furnace, ignoring cyanide, lead or zinc, would be easily salable today at over \$7 per ton of iron produced, and at pre-war prices between \$1 and \$2 per ton of iron.

Any way you look at it the possible values are startling and fully justify the earnest consideration of all furnace operators to the question as to whether their raw material and their method of operation do not present the possibility of exceedingly valuable saving from products which are at present wasted; while raw materials which have hitherto been looked on with disfavor, because of a slight excess of silicious

impurities, may be shown to have a peculiar value on account of the potash which they carry.

I have not been able to check up the actual amount of potash compounds which are at present being lost from operating furnaces, but have made some analyses of the dust which ordinarily is collected in the down-comer, stoves and back of the boilers, and the results are submitted below. It is noted that the higher temperature of the stoves prevents the potash from being deposited. In old times when lower temperatures were the rule it is probable the stove dust ran higher. The material in the down-comer represents largely coke breeze and fine ore with very little of the fume.

WATER SOLUBLE POTASH (K ₂ O) FROM FURNACE DUST.				
	Down-comer.	Boilers.	Stoves.	Flue to stack. Slag.
(1).....	.50%	7.35%	1.45%	
(2).....	.48	7.40	1.33	.36*
(3).....	.02	.009	.02	1.18
(4).....	...	2.75	1.43	
(5).....	.23	1.32	2.27	
(6).....	.57	.87	.80	
(7).....	.30	5.10	1.73	
(8).....		7.00%**		

*Total potash (K₂O).

**Average sample boilers and stoves.

- (1) Low Moor Iron Co., Low Moor, Va.
- (2) Low Moor Iron Co., Low Moor, Va.
- (3) Cleveland-Cliffs Iron Co.
- (4) Cranberry Furnace Co., Johnson City, Tenn.
- (5) Sloss-Sheffield Steel & Iron Co., Birmingham, Ala.
- (6) Alabama Company Ironaton Furnaces.
- (7) Virginia Iron, Coal & Coke Co., Crozer Furnaces, Roanoke, Va.
- (8) Sloss-Sheffield Steel & Iron Co., Sheffield Furnace. Reported by Company.

The boiler dust from the Low Moor furnace carried also about 14 percent zinc.

In addition to the water soluble there were considerable amounts of acid soluble potash.

These figures mean very little, except that the potash is present and in such form that a slight slowing of the speed or lowering of the temperature of the gases causes precipitation to commence. Not only does the dust which is thus incidentally collected represent but a small fraction of the potash in the gases, but it is far less pure and far less concentrated than that which is at present lost.

We now come to the question of collection. Like the automobile, the flying machine and many other things, it is a development and not strictly an invention, even though it may contain many inventions, and lay many inventions under tribute.

It has long been known that dust and fume could be precipitated from gases by means of an electric current of high intensity, and in the last few years the method has been used so extensively and in so many directions as to leave no doubt that it can be successfully applied to the gases from the blast furnace. From a furnace operating standpoint the only thing absolutely necessary is to reduce the temperature of the gases as low as convenient, but not necessarily lower than should be the case anyhow in an efficiently operated furnace, and to pass them through chambers of such cross section that the velocity will be reduced. In other words, it is easy to remove the fumes and

dust from the gases without interfering in any way with the operation of the furnace. The investment would be moderate and the cost of operation of the potash recovery plant would be low, while the gases would be improved for use in the stoves.

Is it not worth while to systematically follow it up?

Not to do so would be as illogical as to build by-product coke ovens and make no effort to save the by-products.

ELECTROLYTIC FORMATION OF PERCHLORATE.*

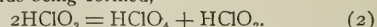
By C. W. BENNETT and E. L. MACK.

The usual conception of the mechanism involved in the anodic formation of perchlorates from chlorates is largely due to Oeschli¹ and his theory has gradually found its way into the text-books of electrochemistry with the result that it is at the present time commonly accepted as representing the actual mechanism of the process.

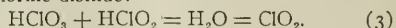
According to this theory the reaction at the anode during chlorate electrolysis is not to be considered a direct addition of oxygen to ClO₃ with the formation of ClO₄ but rather as a more complicated process, during which we must suppose the liberation of the chlorate ion. The various steps involved are, briefly, as follows: Chlorate ion is liberated by the current and, assuming that it acts in a manner analogous to other strongly acid anions, reacts with water at the anode with the formation of free chloric acid and liberation of oxygen,



The free chloric acid generated in this way is probably at a very high concentration in the film of electrolyte which is in immediate contact with the anode. Since in this condition it is known to be very unstable, spontaneous decomposition takes place, perchloric and chlorous acids being formed,

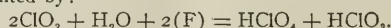


The free chlorous acid thus formed very evidently cannot remain in the solution as such, since in contact with the chloric acid present it would immediately evolve chlorine dioxide:



This evolution of chlorine dioxide has never been observed to take place during this process, and the theory, therefore, assumes that the chlorous acid formed as shown in (2) is immediately oxidized to chloric acid by the oxygen from the decomposition of water by the liberated ClO₃ ions, as shown in equation (1).

The sum total of the reactions which, according to this theory, takes place at the anode may then be represented by:



*Paper presented at the 25th General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

¹Zett. für Elektrochem., 9, 807 (1903).

Oeschli, in order to satisfactorily explain the formation of perchlorate, finds it necessary to assume the liberation of the chlorate ion mainly for the following reasons. Oxygen, when discharged under conditions such that the electrode is reversible, probably requires a lower voltage than that needed for the liberation of oxy-acid anions;² but if we deal with an electrode which is not reversible toward oxygen, that is, where the discharge of oxygen requires a considerable overvoltage, a point may be reached at which the discharge of the oxy-acid anion will become easier, or require a lower voltage, than that for oxygen and will consequently take place. From this standpoint, assuming that ClO_3 is discharged, the formation of perchlorate could be expected to take place only at an anode where the overvoltage for oxygen liberation is sufficient to allow the preferential discharge of the chlorate ion. It is held that this hypothesis is supported by the following facts: (1) Perchlorate formation goes on with a markedly higher efficiency at a smooth platinum anode, where oxygen overvoltage is known to be high, than at an anode of platinized platinum, where oxygen discharge takes place much more easily. (2) If the solution is made alkaline at the anode the efficiency of perchlorate production falls off rapidly; a fact which is explained by the increased ease of oxygen discharge in a solution containing a high concentration of hydroxyl ions. The result is a discharge of oxygen along with the chlorate ions and a consequent drop in the anode efficiency. (3) This hypothesis best explains the rise from a comparatively low efficiency at the beginning of the electrolysis to a higher value as the electrolysis proceeds. When the oxidation is taking place at a high efficiency and the current is interrupted for a short time, it is found, upon closing the circuit, that the efficiency is low just as it was during the first few minutes of the experiment. The idea is that during the break in the current flow the concentration of free chloric acid at the anode falls, largely through diffusion, and that a certain length of time is necessary for the chloric acid to accumulate to that concentration in which it is unstable. During this time oxygen is evolved and the current efficiency necessarily falls. (4) Changing from a smooth platinum anode to one of platinized platinum brings about a marked decrease in efficiency and this is best explained by considering it equivalent to a decrease in current density because of the larger surface presented by the platinized electrode. At this lower current density the efficiency must be lower because we would have more oxygen liberated in proportion to the number of chlorate ions than at the higher current density. Furthermore, many other electrochemical reactions which are commonly considered as being due to anion liberation show this same characteristic of decreased efficiency with platinized anodes. The formation of persulphuric acid and Kolbe's³ synthesis of ethane are

cited as being processes of this type. (5) An increase of temperature, at a fixed current density, brings about a decrease in perchlorate formation and a corresponding increase in oxygen discharge. This is considered to be the result of increase in hydroxyl ion concentration caused by the increased dissociation of water at the higher temperature. (6) Finally, perchlorate formation must be conditioned by chlorate ion discharge since the reaction has not been duplicated chemically; that is, chlorate has not been oxidized to perchlorate by chemical oxidizing agents.

This theory is open to the objection that it rests upon several assumptions which may or may not be true. We have no direct evidence that chloric acid, when sufficiently concentrated, decomposes with the formation of perchloric and chlorous acids. The visible products of the decomposition are known to be perchloric acid, chlorine dioxide, chlorine and oxygen. While the intermediate formation of chlorous acid is possible it has not, up to this time, been demonstrated satisfactorily. If we are to reason from analogy to the reaction which takes place when alkali chlorates are heated⁴ it would appear much more probable that the primary decomposition products would be perchloric and hydrochloric acids.

Granting, however, that the liberated chlorate ion and free chloric acids would act in the manner assumed, the theory is still unsatisfactory in that it does not explain the decrease in yield of perchlorate on substitution of platinized for smooth platinum anodes or the marked fall in efficiency with rising temperature. In the former case, using a platinum anode a current efficiency of 97.0 percent was noted,⁵ while with a platinized anode, the other conditions remaining unchanged, the efficiency dropped to 2.7 percent. It is very evident that it would be necessary to assume a tremendous decrease in current density to account for the marked efficiency drop at the platinized anode since a succeeding experiment shows that, under like conditions, using a smooth platinum anode and a current density approximately one-fourth that in the first experiment cited, the efficiency fell only to 92.0 percent.

Regarding the temperature effect it may be stated with certainty that the increase in the dissociation of water with a temperature rise of 73° is insufficient to account for a decrease in efficiency of 97 percent. The efficiency at 7° is 97 percent, while no perchlorate is formed at 80°C. , other conditions remaining unchanged.

It has seemed advisable, therefore, to postulate that the electrolytic formation of perchlorate does not depend upon the liberation of the chlorate ion but rather is to be considered as a direct addition of oxygen to the chlorate ion. The object of this paper is to show that the phenomena observed during perchlorate for-

²Rose: *Zeit. für Elektrochem.*, 5, 169 (1898).

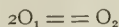
³Liebig's *Ann.*, 69, 257 (1849).

⁴Oeschli: *loc. cit.*, pp. 812 and 818.

⁵Cf. Seobal: *Zeit. phys. Chem.*, 44, 319 (1903).

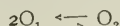
mation are most easily and satisfactorily accounted for from this viewpoint. It is further proposed to furnish independent proof that chlorate may be oxidized to perchlorate by strictly chemical means; that is, under conditions where the liberation of chlorate ion cannot be assumed.

Let us consider for a moment the conditions existing at an insoluble anode during electrolysis of solutions containing oxygen or hydroxyl ions. Recent investigations⁶ have shown that the action of the electrolyzing current is to liberate oxygen in the active or atomic form. This oxygen unless depolarized by some substance present at the anode will be converted into molecular or gaseous oxygen, the reaction represented by:



Further, it has been pointed out that the rate of this reaction, and consequently the concentration of active oxygen, or O_1 , which is present at the anode at any given time, is dependent upon (1) the nature of the anode material, (2) the current density, (3) temperature, (4) nature of the solution, and (5) the elapsed time of electrolysis.

Schoch⁷ has pointed out that only an *exceedingly small voltage* is required to discharge oxygen or any other ion into an electrode which is absolutely free from electromotively active material, and it follows from this and the above statement that the potential of the anode, at any given time, in a solution capable of discharging oxygen, depends primarily upon the concentration of active oxygen then existent at the electrode. Thus we see that by properly varying the conditions we may have oxygen discharged at any potential above a certain minimum value which is determined by the equilibrium value of the equation



at the particular anode and under the particular conditions in question.

It may be well to point out here that in order to oxidize a given substance present in the electrolyte, chlorate for instance, it is necessary that the potential of the anode should rise *not to that point necessary to bring about the liberation of gaseous oxygen*, as is commonly believed, *but only to that point necessary to produce a concentration of active oxygen sufficient to oxidize the chlorate ion*. That this is the case and that the potential necessary for the latter process is very much less than that required for the former is conclusively shown by the work of Schoch.⁸ Using a N/3 potassium chlorate solution and an iron anode it was found that the formation of perchlorate began when the anode potential reached + 0.023 volts,⁹ while a succeeding experiment showed that at an iron anode

oxygen is not evolved until an anode potential of + 1.5 volts is reached.

This experiment, even without the support of further evidence, shows that the formation of perchlorate is not determined by the liberation of chlorate ion since no one would claim for this ion a discharge potential as low as + 0.023 volts. Most of the attempts at measurement have obtained values around + 1.37 volts.¹⁰

Having thus shown that perchlorate can be produced at an anode potential far below that required for the liberation of oxygen as well as much below that commonly assigned for ClO_3 discharge, let us consider the phenomena actually observed during the electrolysis of a chlorate solution, assuming the formation of perchlorate to be the result of a direct addition of oxygen to the chlorate ion.

Using a smooth platinum anode in a strong neutral chlorate solution with a current density of, say, 4 to 6 amperes per square decimeter, we find the efficiency of perchlorate formation to be high, possibly as high as 95 percent. The anode potential is also found to be high and from the standpoint taken we consider that we now have at the anode active oxygen in such concentration that it is able to oxidize the chlorate ion rapidly and with good efficiency. We know that we are here dealing with an anode which exhibits a high overvoltage. This means that the concentration of active oxygen is above the equilibrium value. If we decrease the current density below the value first taken, we find a decrease in current efficiency with respect to perchlorate formation and a corresponding decrease in anode potential. This becomes intelligible when we consider that at moderate current densities oxygen overvoltage, and consequently concentration of active oxygen, decreases¹¹ with decrease of current density. Again, if the temperature be raised, we find the current efficiency decreases markedly. This, again, is in accord with the view taken since we have seen that the concentration of active oxygen present at the anode at any given time is dependent upon the state of the equilibrium

active oxygen $\rightleftharpoons$ oxygen molecule.

Increased temperature tends to shift this equilibrium in favor of molecular oxygen and we would expect, therefore, a lower active oxygen concentration and consequently a lower oxidizing power. A sufficiently high current density at the higher temperature would, however, tend to increase the rate of production of active oxygen and increase its concentration in the electrode. As the current density is increased, we should therefore expect to obtain a consequent rise in efficiency of chlorate oxidation tending to overcome the inhibitory effect of the high temperature. This is actually realized experimentally.¹² The current density used was 16 amperes per square decimeter and with

⁶Bennett and Thompson: Trans. Am. Electrochem. Soc., 29, 15 (1916).

⁷Jour. Phys. Chem., 14, 665 (1910).

⁸Jour. Phys. Chem., 14, 735 (1910).

⁹All potentials given in this paper are the observed readings against the normal calomel electrode. The signs are those observed in the experimental arrangement. This is in accord with the suggestion of Luther. See Le Blanc: Textbook of Electrochemistry, 4th Ed., 245.

¹⁰Le Blanc: Zeit. phys. Chem., 8, 299 (1891).

¹¹Bennett and Thompson: loc. cit.

¹²Oeschil: loc. cit., p. 817.

the solution maintained at 80° gave a current efficiency of 13.5-14.8 percent. This was raised to 40.0-42.5 percent when the current density was increased to 20.8 amperes per square decimeter, the temperature remaining constant at 80° .

If the solution is made alkaline the current efficiency falls off rapidly, a fact which is explained without difficulty when we recall that the discharge potential for oxygen at platinum is lower¹³ in alkaline than in acid solutions. In other words, the active oxygen concentration is lower. Furthermore, oxidizing power in general is lower in alkaline than in neutral or acid solutions. This is to be concluded from the fact that many oxidations which take place readily in acid solution are either entirely prevented or proceed at a very much decreased rate when the solution is made alkaline.

It is noted that on starting the electrolysis both the potential of the anode and the efficiency are somewhat below their normal values. Both, however, steadily increase to a maximum with increasing time. This is entirely to be expected from the fact that reliable measurements of anodic overvoltage¹⁴ always indicate a low concentration of active oxygen during the first few moments of oxygen discharge.

Finally, on substituting an anode of platinized platinum for one of polished platinum, other conditions remaining constant, we find a notable decrease in anodic efficiency. This, once more, is satisfactorily explained from our viewpoint, since the work of Coehn and Osaka¹⁵ interpreted from the viewpoint which we have taken shows that at a given current density we must have a lower concentration of active oxygen at a platinized anode than at one of smooth platinum. Their results¹⁶ gave for the potential of oxygen at smooth platinum + 1.39 volts, and at platinized platinum + 1.19 volts.

From what has been said above, it becomes evident that we can satisfactorily account for the anodic formation of perchlorate without assuming anything at all about the liberation of the chlorate ion by considering that the oxidation is dependent only upon the presence at the anode of a sufficient concentration of active oxygen. It has been satisfactorily shown that this concentration corresponds to an anodic potential far below that required for liberation of gaseous oxygen and nearly as far below that required for the liberation of the chlorate ion, if we are to accept for this the values given by the best measurements available.

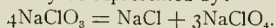
Although it may be readily admitted that the potential of the anode during the electrolysis of a chlorate solution is at all times probably above that necessary for chlorate discharge, it must be kept in

mind that these reactions will not take place as long as we have chlorate present in sufficient concentration. This follows since it has been shown that the direct oxidation of the ClO_3 is the more easily accomplished process; that is, the one requiring the lowest potential, and as such will take place first. This does not mean that the oxidation will take place under all conditions with high efficiency since we have seen that those factors which unfavorably affect this reaction are exactly those which tend to lower the concentration of active oxygen at the electrode. The direct result of this decrease is a decrease in its ability to oxidize chlorate and a corresponding increase in the ease of oxygen evolution and the consequent drop in current efficiency with respect to perchlorate formation.

EXPERIMENTAL.

Although the theory outlined above is well supported by known facts, it seemed desirable to have independent proof of the fact that chlorates may be directly oxidized to perchlorates by chemical means and under conditions such that the liberation of the ClO_3 ion cannot be assumed.

We have evidence that this is true in the fact that chlorates when heated to moderate temperatures produce perchlorates, one portion of the chlorate furnishing oxygen for the oxidation of another portion; a reaction which may be represented by:



The possibility of a direct oxidation was even more strikingly shown by Fowler and Grant.¹⁷ They found on heating chlorate with silver oxide that the chlorate was completely converted to perchlorate without the loss of oxygen, metallic silver being the other product.

It was desired, however, to show that the oxidation could be brought about in an aqueous solution and for this purpose several oxidizing agents were selected as the most useful and their action on sodium chlorate investigated as described below.

Methods of Analysis.

The method used for determining the amount of the various chlorine acids in the presence of each other was essentially that described by Treadwell-Hall¹⁸ and is briefly as follows: In a solution containing chlorides, chlorates and perchlorates, or the corresponding free acids, the amount of chlorine as chloride was determined directly by titration of one sample (1). A separate portion (2) titrated, after reduction with ferrous sulphate with an excess of dilute sulphuric acid, gave the amount of chlorine as chlorate plus that as chloride. A third portion (3) of the solution after evaporation to dryness with sodium carbonate was fused in a tall platinum crucible, the mouth being closed by a plug of loosely packed asbestos fibre. This sample showed the total amount of chlorine present in all forms. The amount of chlorine present in the original solution is, then, shown by (1), that as chlo-

¹³Smale: Zeit. phys. Chem., 14, 577 (1894).

¹⁴Foerster and Piguet: Zeit. für Elektrochem., 10, 714 (1904).

¹⁵Zeit. anorg. Chem., 34, 86 (1903).

¹⁶The measurements given by them were made against a normal hydrogen electrode, but for the sake of consistency in this paper these have been converted to the normal calomel electrode values.

¹⁷Jour. Chem. Soc., 57, 272 (1890).

¹⁸Analytical Chemistry, p. 463 (1911).

rate by the difference between that found in (2) and (1), and that present as perchlorate by the difference between the amount shown by (3) and (2).

The amount of chlorine in these samples was in all cases determined¹⁹ by addition of an excess of tenth normal silver nitrate solution, filtering off the precipitated silver chloride and titrating the excess silver nitrate with a tenth normal solution of ammonium sulphocyanate, using ammonium ferric alum as indicator. This method was found to be rapid and gave consistent and very accurate results. Duplicate samples containing 0.3 gram chlorine frequently gave results differing by only 0.3 milligram.

In addition to the quantitative determination all solutions were examined for the presence of perchlorates by the micro-chemical test described by van Breukeleveen.²⁰

Experiments with Persulphate.

The first oxidizing agent studied was sodium persulphate. This is commonly considered as a very powerful oxidizing agent and it seemed probable that it might convert chlorate to perchlorate even in aqueous solution. This was established as true by the following experiments.

Preliminary Experiment: A solution containing about 5 percent of sodium chlorate was boiled for ten minutes with an excess of sodium persulphate. After evaporation to dryness concentrated hydrochloric acid was added and the solution again evaporated, on a water bath, to convert all remaining chlorate to chloride. After dissolving the residue in water, silver nitrate was added until all chloride present was removed. After filtering the solution was evaporated, the residue fused with sodium carbonate, dissolved in dilute nitric acid and silver nitrate added. A heavy precipitate of silver chloride indicated that a portion of the chlorate originally present had been converted to perchlorate.

Experiments 8-12: One-gram portions of sodium chlorate, representing 0.3324 gram chlorine as chlorate, were boiled with solutions of sodium persulphate; the conditions being as shown below. In all cases a considerable oxidation to perchlorate was found. Tests of the several solutions for chlorides, after boiling with persulphate, showed the absence of chlorine in this form. We have to deal with chlorine as chlorate and perchlorate only. The latter was determined by difference, as in the first experiments.

	8	9	10	11	12
Chlorine (as chlorate) taken.....	0.3324	0.3324	0.3324	0.3324	0.3324
Water—cc.	100	100	100	25	25
Sodium persulphate (grams)	10	10	10	10	10
Length of time heated (minutes)	30	30	60	30	30
Chlorine (as chlorate) found.....	0.2710	0.2705	0.2736	0.2730	0.2751
Percentage oxidized to perchlorate	18.47	18.32	17.69	17.87	17.24

While these experiments showed in a satisfactory manner that chlorate may be oxidized to perchlorate by means of persulphate, it was desired, if possible,

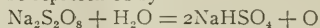
to establish conditions under which the oxidation would take place more efficiently, since it was noted that a large amount of oxygen was evolved during the reaction in the previous experiments. It has been pointed out²¹ that the presence of silver salts seems to affect favorably the oxidizing power of persulphates, many substances being easily oxidized in this manner which are scarcely affected by persulphate alone.

Experiment 26: One cc. of tenth normal silver nitrate was added to a solution containing one gram sodium chlorate in 25 cc., representing 0.3324 gms. Cl, and 10 gms. sodium persulphate. Boiled one-half hour.

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment..	0.2565 grams
Oxidized to perchlorate	0.0759 grams
Oxidized to perchlorate	22.83 per cent

This experiment confirmed the fact that the presence of even small amounts of silver salts increased the oxidizing power of persulphates. Since this phenomenon has been ascribed to the fact that silver salts catalytically increase the velocity with which persulphate decomposes, and since this decomposition may be represented by



it seemed probable that under conditions such that the sulphate ion would be removed from the sphere of reaction as fast as formed, the velocity of decomposition and the oxidizing power might be favorably affected. This was confirmed as follows:

Experiment 31: A solution, containing in 100 cc., one gram sodium chlorate, 10 grams sodium persulphate and 13 grams barium oxide was boiled for 30 minutes. After removal of the barium sulphate, an analysis gave the following results:

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment ...	0.2202 grams
Oxidized to perchlorate	0.1122 grams
Oxidized to perchlorate	33.75 per cent

Although it seemed certain that in the previous experiments the oxidation was due solely to the persulphate present, the statement is frequently made that dilute solution of chloric acid or weakly acid solutions of chlorates are somewhat oxidized to perchlorate on boiling. To determine whether this was true for the conditions employed in the experiments described two solutions were made up containing in 25 and 100 cc. respectively an amount of sulphuric acid and of sodium sulphate corresponding approximately to the end products of decomposition of 10 grams sodium persulphate; that is, 6 grams sodium sulphate and 2.1 cc. concentrated sulphuric acid. To each of these one gram sodium chlorate was added and the solution boiled for 15 minutes. Neither the usual analysis nor the micro-chemical test showed the presence of perchlorate in either solution after this

¹⁹Sutton: Volumetric Analysis, 9th Ed., p. 172.

²⁰Rec. Trav. chim. Pay-Bas., 17, 94 (1898).

²¹Price: Per Acids and Their Salts, p. 35 (1912).

treatment. This shows conclusively that the oxidation obtained in experiments previously described is to be assigned to the sodium persulphate.

In all cases described the micro-chemical test²² showed the presence of considerable quantities of perchlorate. It seemed desirable, however, to determine analytically the quantity of perchlorate present. This was done as follows:

Experiment 40. One gram sodium chlorate, containing 0.3305 gram Cl as chlorate, added to 10 grams sodium persulphate in 25 cc. water. Boiled 30 minutes.

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment...	0.2886 grams
Total chlorine found after treatment	0.3312 grams
Oxidized to perchlorate	0.0626 grams
Oxidized to perchlorate	18.94 per cent

These experiments establish satisfactorily that chlorate can be oxidized to perchlorate by means of sodium persulphate.

Experiments with Ozone.

Although the action of ozonized oxygen on solutions of chlorates was investigated by Oeschli,²³ the result of his experiments is hardly conclusive, since one case in which a 2.5 percent sodium chlorate solution was saturated with ozonized oxygen for 8 hours, showed a decrease of 1.2 percent in the chlorate content. A following experiment in which free chloric acid was substituted for the sodium chlorate, gave a decrease of 0.34 percent in chlorate as a result of the treatment with ozone. The conclusion reached, however, was "das eine Oxydation des ClO_3 Ions durch ein etwa 6 Volumprozent Ozon enthaltendes Gas nicht bewirkt werden kann."

It seemed desirable, therefore, to carry on experiments with ozone in order to determine whether a larger proportion of the chlorate might not be oxidized by this means.

Experiment 25: Ozonized oxygen for this experiment was generated by passing dry oxygen through a Siemen ozonizer, the high tension current being supplied by a 10,000 volt transformer of 1 KVA capacity. The gas thus generated was bubbled through the chlorate solution contained in a large test tube, the length of the experiment being 19 hours and the temperature of the solution 22°. The solution contained 1 gram chlorate and 1 cc. sulphuric acid (Sp. gr. 1.82) in 25 cc.

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment..	0.3298 grams
Oxidized to perchlorate	0.0026 grams
Oxidized to perchlorate	0.78 per cent

Since it is known that silver oxide decomposes ozone catalytically, it was thought that the presence of this substance might have a favorable effect on the oxidizing power. This seemed especially probable in view of the increased oxidation obtained with persulphate through the presence of silver salt.

Experiment 28: Solution consisted of one gram sodium chlorate, 1 cc. of normal nitric acid, 0.10 gram silver oxide and 25 cc. water. Ozonized oxygen was bubbled through the solution for 20 hours, the temperature of solution being 22° C. Results of analysis follow:

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment..	0.3262 grams
Oxidized to perchlorate	0.0062 grams
Oxidized to perchlorate	1.86 per cent

Experiment 32: The solution used was the same as in the previous experiment but was maintained at 100° C. Ozonized oxygen was passed through the solution for 5 hours. Result of analysis follows:

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment..	0.3301 grams
Oxidized to perchlorate	0.0023 grams
Oxidized to perchlorate	0.69 per cent

Although no attempt was made in the previous experiments to regulate the ozone concentration of the ozonized oxygen used, it was known to be about 7 percent by volume. It seemed probable that a gas with higher ozone concentration might be more effective in obtaining the desired oxidation. An apparatus was therefore constructed which was capable of producing oxygen containing a very high percentage of ozone. The ozone was produced by electrolysis of sulphuric acid solutions at low temperatures. The apparatus employed was essentially a modification of that described by Fischer and Massenay.²⁴

No attempt was made to control the concentration of ozone produced by this apparatus, but it continuously furnished a gas of very much higher content than that from the Siemens tube. One analysis showed a concentration of 21 percent ozone by volume.

Experiments 38 and 39: Solutions containing one gram sodium chlorate and 2 cc. sulphuric acid (Sp. gr. 1.82) in 25 cc. water were used and were maintained at 100° by means of water bath. Ozonized oxygen produced by the apparatus described was allowed to bubble through these solutions for two hours. As in the previous cases a slight oxidation of the chlorate was obtained.

Analysis.

	No. 38	No. 39
Chlorine (as chlorate) taken	0.3324	0.3324
Chlorine (as chlorate) found after treatment	0.3300	0.3296
Oxidized to perchlorate	0.0024	0.0028
Oxidized to perchlorate	0.72%	0.82%

The experiments with ozone show, therefore, that while ozone is capable of oxidizing acid solutions of chlorates, the oxidation is not at all efficient. In all cases described the amount of ozone used was in excess of the theoretical amount necessary to oxidize all chlorate present. It may be pointed out that while the amount oxidized is small it is nevertheless certain that perchlorate was produced since the micro-chemical test showed, unquestionably, the presence of perchlorate in all solutions after treatment with ozone.

Since acid solutions of permanganates are known

²²Van Breukeleveen, loc. cit.

²³Loc. cit., p. 821.

²⁴Zeit. anorg. Chem., 52, 202, 229 (1907).

to be strong oxidizing agents, this was the next material studied.

Experiment 45: A solution containing one gram sodium chlorate, 1 cc. sulphuric acid (Sp. gr. 1.82) and one gram potassium permanganate in 100 cc. water was boiled for 30 minutes. The solution showed no perchlorate present.

Analysis.

Chlorine (as chlorate) taken 0.3324 grams
Chlorine (as chlorate) found after treatment.. 0.3326 grams

This experiment shows that acid solutions of potassium permanganate will not oxidize chlorate to perchlorate.

The next oxidizing agent studied was aqueous sodium peroxide.

Experiment 46: A solution containing one gram sodium chlorate and 10 grams sodium peroxide in 25 cc. was boiled for 15 minutes. After cooling and diluting to 100 cc. the solution was acidified with dilute nitric acid.

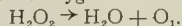
Analysis.

Chlorine (as chlorate) taken 0.3324 grams
Chlorine (as chlorate) found after treatment.. 0.3317 grams

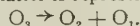
The slight discrepancy noted here between the amount of chlorate taken and that found after treatment is probably to be regarded as experimental error since the micro-chemical test used failed to show the presence of perchlorate. The amount represented by the difference in the two chlorine determinations is probably within the experimental error in this case since the presence of large amounts of sodium salts in the solution made the analysis somewhat less accurate than in previous cases.

EXPERIMENTS WITH HYDROGEN PEROXIDE.

Hydrogen peroxide is probably to be considered as one of the strongest of oxidizing agents since its decomposition must be accomplished by the generation of atomic or active oxygen:



Although not commonly so considered it should be a stronger oxidizing agent than ozone since the decomposition of the latter is represented by:



The concentration of active oxygen in the case of the hydrogen peroxide is thus seen to be much higher. Consequently its oxidizing power must be correspondingly greater.

The action of hydrogen peroxide on chlorate solutions was therefore next investigated.

Alkaline solutions of hydrogen peroxide were used as oxidizing agents. A solution containing one gram sodium chlorate and 1 cc. ammonium hydroxide (Sp. gr. 0.90) in 15 cc. perhydrol was boiled for 30 minutes. Analysis of the solution gave the following results:

Analysis.

Chlorine (as chlorate) taken 0.3305 grams
Chlorine (as chlorate) found after treatment.. 0.3298 grams

No perchlorate could be found in the solution by microscopic test. The experiment therefore shows

that alkaline hydrogen peroxide is not a sufficiently powerful oxidizing agent to convert chlorates to perchlorates.

Experiment 47: One gram of sodium chlorate was dissolved in 15 cc. perhydrol (Merck's 30 per cent) and the solution evaporated to dryness on the water bath. The residue was dissolved in a second 15 cc. portion of perhydrol and again brought to dryness. After dissolving the residue in water the following analysis was obtained:

Analysis.

Chlorine (as chlorate) taken 0.3324 grams
Chlorine (as chlorate) found after treatment.. 0.3327 grams

This experiment shows that chlorate in neutral solutions is not oxidized to perchlorate by 30 per cent hydrogen peroxide.

It is undoubtedly true that oxidizing agents, in general, are more powerful in the presence of acid than in neutral or alkaline solutions. Therefore it was decided to investigate the action of hydrogen peroxide on acid solutions of chlorates. Some work has been done along this line by Tanatar²⁵ who investigated the action

²⁵Ber., 32, 1013 (1899).
of hydrogen peroxide on halogen oxy-acids. He found that hydrogen peroxide had no effect on either neutral or acid solutions of chlorates, while bromates were quickly reduced to bromide with evolution of some bromine. These conclusions are certainly in error in so far as they state that acid chlorate solutions are unaffected by hydrogen peroxide. This will be seen from the following experiments:

Experiment 48: One gram sodium chlorate was dissolved in 25 cc. of 30 per cent hydrogen peroxide which had previously been acidified by 1 cc. sulphuric acid (Sp. gr. 1.82). The solution was boiled for one hour. Soon after the solution had reached the boiling point a yellow gas was evolved. This was at first thought to be chlorine but more careful examination showed it to be a mixture of chlorine dioxide and chlorine. The microchemical test showed the presence of perchlorate in the solution and analysis gave the following results:

Analysis.

Chlorine (as chlorate) taken 0.3324 grams
Chlorine (as chloride) found after treatment.. 0.2916 grams
Chlorine (as chlorate) found after treatment.. 0.0030 grams
Total chlorine found after treatment..... 0.2927 grams

This experiment shows that chlorate, through the action of acid solutions of hydrogen peroxide, is largely converted to chloride. A considerable amount of chlorine and chlorine dioxide is evolved at the same time.

Experiment 49: The conditions in this experiment were the same as in the previous case with the exception that 3 per cent hydrogen peroxide was used. The solution was boiled for 12 hours.

Analysis.

Chlorine (as chlorate) taken 0.3324 grams
Chlorine (as chloride) found after treatment.. 0.0122 grams
Chlorine (as chlorate) found after treatment.. 0.3162 grams

This experiment, again, shows that by the action of acid hydrogen peroxide solutions on chloride we have

apparent reduction to chloride. This was confirmed by a series of experiments which all gave results similar to those described above.

It now became necessary to account for the *apparent* reducing action which hydrogen peroxide exerted on acid chlorate solutions. The fact that chlorine and chlorine dioxide were set free during this reaction caused no difficulty. The presence of a small amount of hydrochloric acid in the solution would be sufficient to account for this, since it is known that hydrochloric acid solutions rapidly decompose chlorate, particularly when heated to 80°. This decomposition may be represented by



It seemed certain, therefore, that the main reaction with which we were dealing was an apparent reduction of chloric to hydrochloric acid, and that the evolution of chlorine and chlorine dioxide was to be considered as a secondary reaction due to the action of hydrochloric acid on chlorate, which still remained undecomposed.

To account for the apparent reducing action shown here by hydrogen peroxide several possibilities presented themselves. It seemed improbable that so strong an oxidizing agent as hydrogen peroxide was here acting as a reducing agent, especially in view of the fact that many, if not all, of the apparent reductions accomplished by hydrogen peroxide are in reality the result of oxidations to higher instable oxides²⁶ which immediately decompose if the experiment is conducted under ordinary conditions. Applying this idea to the case in question it was considered possible that the chloric acid was oxidized by hydrogen peroxide to a higher form, which was unstable under ordinary conditions. Since the acid next higher than chloric acid is perchloric acid and this was shown to be perfectly stable under the conditions existing in the experiments it was necessary to assume the formation of an acid still higher than perchloric. The further assumption necessary was that this hypothetical higher acid would decompose spontaneously with the liberation of oxygen and formation of hydrochloric acid.

Assuming for the moment the existence of this compound it seemed highly probable that during its formation from chloric acid we would pass through the perchlorate stage, or, in other words, that it should be formed equally well from perchloric acid.

A preliminary experiment showed, however, that this theory was untenable. A 5 per cent solution of potassium perchlorate acidified with sulphuric acid was added to an equal volume of 30 per cent hydrogen peroxide and the whole boiled for 10 minutes. No chlorides were present in the solution after this treatment. This experiment is supported by the work of Tanatar²⁷ who found that perchloric acid is not affected by hydrogen peroxide. It became necessary, therefore, to abandon the position first taken.

The possibility next considered was the existence of a molecular compound between chloric acid and hydrogen peroxide. No assumptions were made as to the nature of this hypothetical compound, but for the time being it was considered analogous to the possible compounds between ferrous sulphate and hydrogen peroxide described by Mummery.²⁸ The hypothesis which we are now considering postulated, of course, that this compound $\text{HClO}_3 \cdot x \text{H}_2\text{O}_2$ if existent, would decompose with formation of hydrochloric acid.

If this compound were actually formed on mixing solutions of chloric acid and hydrogen peroxide it seemed probable that its presence would be revealed by a measurable thermal change. Accordingly the heat of dilution of solutions of chloric acid with hydrogen peroxide was determined as follows:

Experiment 50: The apparatus used consisted of a silvered Dewar flask of about 200 cc. capacity, fitted with a stopper carrying a small funnel tube and a 100° thermometer, graduated in 0.1°. The stopper was also cut away at one side to permit the introduction of a glass stirring rod.

Twenty cc. of a 5 per cent chloric acid solution was introduced into the flask and the temperature allowed to become constant. 5 cc. 30 per cent hydrogen peroxide solution were then brought to the same temperature and introduced into the flask. The temperature of the mixture rose rapidly and reached a value where it remained constant for several minutes. The thermal effect on diluting 20 cc. of 5 per cent chloric acid with 5 cc. of water was next determined, the procedure being exactly similar to that used in the previous case. The data obtained was as follows:

Initial temperature of chloric acid	24.70°
Initial temperature of hydrogen peroxide	24.70°
Maximum temperature of mixture	24.95°
Rise in temperature of mixture	0.25°
Initial temperature of chloric acid	24.55°
Initial temperature of water	24.55°
Maximum temperature of mixture	24.80°
Rise in temperature of mixture	0.25°

These experiments are sufficient to indicate that there is little possibility of the formation, at room temperature, of a compound of chloric acid and hydrogen peroxide. One possibility remained to be considered, however, before abandoning this hypothesis. It has been mentioned that the apparent reducing action of hydrogen peroxide on chloric acid does not become evident until a temperature of about 80° is reached. The possibility existed, therefore, that the intermediate compound just considered might be formed at a point somewhat above room temperature. If this were true the formation of the compound would be indicated by a break in the heating curve of a mixture of chloric acid and hydrogen peroxide. An investigation of the heating curve of a 5 per cent chloric acid solution mixed with an equal volume of 30 per cent hydrogen peroxide failed to show any break which would indicate the formation of a compound.

The conclusion was therefore reached that the *ap-*

²⁶This will be discussed more fully in a later paper.
²⁷Loc. cit.

²⁸Jour. Soc. Chem. Ind., 32, 889 (1913).

parent reduction of chlorate to chloride by hydrogen peroxide could not be assigned to the formation of an instable compound between the two.

The most satisfactory explanation of this phenomenon, however, was found in the fact that in a dilute solution of chloric acid we have a small amount of chlorine liberated through spontaneous decomposition of the acid. This chlorine, by its action on the hydrogen peroxide immediately forms hydrochloric acid.²⁹ The hydrochloric acid thus produced would, of course, immediately attack the remaining chlorate, the products of this reaction being hydrochloric acid, chlorine, chlorine dioxide, and oxygen. The reaction is therefore auto-catalytic, and a small amount of hydrochloric acid is sufficient to start the decomposition. It has been mentioned that the formation of chlorides in a solution of chloric acid and hydrogen peroxide, does not begin to be appreciable until the temperature is raised to about 80°. This is in accord with the work of Sand,³⁰ who investigated the reaction between chloric acid and hydrochloric acid. He found that the velocity of the reaction became appreciable at temperatures above 70°.

This explanation of the apparent reducing action of hydrogen peroxide in chloric acid has the advantage that it makes no assumption whatever but uses only well known facts to account for the phenomenon. There is scarcely room for doubt that the explanation put forward represents the true mechanism of the reaction. It also shows that hydrogen peroxide does not here act as a reducing agent, in the true sense of the term.

EXPERIMENTS WITH ACTIVATED OXYGEN.

The fact that oxygen is activated or ionized by ultra-violet light rays is well established.³¹ In this condition it is a very powerful oxidizing agent, probably stronger than either ozone or hydrogen peroxide. The action of activated oxygen on chloric acid was therefore investigated.

It is frequently stated that solutions of chloric acid are slowly oxidized on standing in sunlight. While this is probably true the necessity for the presence of oxygen has not been recognized.

A solution was made up containing 0.4784 gram sodium chlorate and 0.25 cc. sulphuric acid (Sp. gr. 1.820) in 45 cc. This represented 0.1582 gram chlorine as chlorate. The solution was placed in a transparent quartz flask and a neutral atmosphere maintained by continuously passing in nitrogen which had been freed from traces of oxygen by washing with alkaline pyrogallol solution. Ultra-violet light was obtained by means of a Copper Hewitt quartz tube mercury arc lamp, the flask containing the solution being suspended about 5 cm. from the lamp. The experiment continued for 28 hours. No oxidation of the chlorate took place, as is shown by the analysis.

Analysis.

Chlorine (as chlorate) taken 0.1582 grams
Chlorine (as chlorate) found after experiment. 0.1580 grams
This experiment shows conclusively that, in the absence of oxygen, dilute chloric acid solutions are not photo-chemically oxidized to any appreciable extent.

The next experiment was similar to the preceding one, except that oxygen was continuously bubbled through the solution. The flask held 50 cc. of solution containing 1.000 gram of sodium chlorate and 0.50 cc. of sulphuric acid (Sp. gr. 1.820). This represents 0.3305 gram chlorine as chlorate. The solution was subjected to the action of the ultra-violet rays for 8 hours. After the treatment, the micro-chemical test showed perchlorate to be present. This was confirmed by analysis.

Analysis.

Chlorine (as chlorate) taken 0.3305 grams
Chlorine (as chlorate) found after experiment. 0.3269 grams
Oxidized to perchlorate 0.0036 grams
Oxidized to perchlorate 1.09 percent

It was desired to determine whether more of the chlorate could be oxidized by longer treatment with the activated oxygen.

Accordingly, a solution of sodium chlorate was made up and found, by analysis, to contain 0.1172 gram in 10 cc. The solution was acidified slightly (0.5 per cent) with sulphuric acid. The other conditions being as in previous experiments the solution was subjected to the ultra-violet rays, oxygen being continuously bubbled through. 10 cc. samples, for analysis, were withdrawn at regular intervals. The results follow:

Time elapsed (hours)	Sodium chlorate found per 10 cc. solution
0	0.1172
24	0.1158
72	0.1160
96	0.1157

It will be noted that during the first 24 hours a small amount of the chlorate was oxidized. This represents about 1.1 per cent of the total amount present. During the remaining time no further oxidation took place. It will also be noted that these results are practically identical with those obtained when ozonized oxygen was used as the oxidizing agent. It is probable that we have only a very low concentration of active oxygen in both cases and that it is not at all comparable, in degree, to that present at the anode during electrolysis. Consequently it is necessary to assume that, using active oxygen in these low concentrations, an equilibrium of some kind is established when about 1 per cent of the chlorate present has been oxidized. It seems very probable that if this concentration of active oxygen be increased a further oxidation would result.

It is held, however, that the conditions maintained in the above experiments duplicate (qualitatively) those existing at the anode during chlorate electrolysis and show that perchlorate can be formed by the direct addition of oxygen to the chlorate radicle.

CONCLUSIONS.

1. Chlorate may be oxidized to perchlorate by persulphuric acid, ozone, and hydrogen peroxide in acid solutions.

²⁹Fairley: Jour. Chem. Soc., 31, 22 (1877).

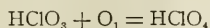
³⁰Zeit. phys. Chem., 50, 465 (1904).

³¹Sheppard, Photo-chemistry, p. 253 (1914).

2. In the case of hydrogen peroxide the hydrochloric acid formed interferes with the reaction.

3. This oxidation may also be carried on with oxygen activated by ultra-violet light.

4. The reaction is considered to take place according to:



the quantity of oxidation depending on the concentration of active oxygen present.

5. Since active oxygen chemically produced oxidizes chloric acid to perchloric acid and since active oxygen is formed at the anode it follows that the electrochemical formation of perchlorate is the result of direct oxidation.

6. Perchlorate is formed at the anode at a potential, far below that necessary for the continuous discharge of any ion present in the solution.

7. The conditions realized in the experiments described above duplicate, qualitatively, those existing at the anode during electrolysis.

A PRACTICAL METHOD OF DETERMINING THE SPECIFIC GRAVITY OF VARIOUS SAMPLES OF TIMBER.*

By K. HV. KNUDSEN.

Every practical manufacturer of pulp will have noticed differences in the yield of cellulose from the same wood, but few know accurately, if at all, how large these fluctuations may be. It is usually inconvenient, and often a matter of great difficulty to determine separately the yield of raw materials from different sources.

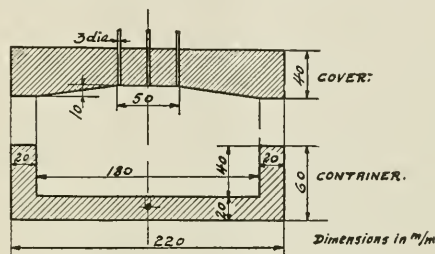
A glance at a transverse section of a log suffices to show that the wood is not uniform; it consists of alternating concentric layers of a more and a less dense nature, the varying width of the layers furnishing an index of the relative rate of growth of the timber.

With a view of throwing some light on the relations between the growth of the tree and yield of pulp the following laboratory experiments were undertaken. A few disks about 2 cm. thick were sawed off from various logs and then allowed to dry out in the air for a couple of weeks and finally analyzed for their cellulose content.

Of the many methods suggested for the determination of cellulose no single one is adapted to highly dignified materials. Cross and Bevan's chlorination method¹ is by far the most suitable one, but nevertheless, it shows in a minor degree the errors inherent in other practical processes, i. e., it is necessary to choose between an imperfectly purified cellulose on the one hand, and a loss of cellulose, under the action of the reagents on the other. In addition to this handicap it is always difficult to select a sample representing a true average.

Dean and Tower² softened the wood in boiling water and sampled by rasping lightly; they dried the sample in the air and finally freed it from large splinters and sawdust. This, however, is too tedious a process for practical purposes. Instead it was attempted to get a fair sample from the sawdust from a diametrical cut through the disks. A separate moisture test was made of each sample, after it had been airdried; and 1 to 2 gm. was taken for the cellulose determination.

The chlorination method mentioned was applied in a modified form as described by Renker and Schwalbe in *Die Chemie der Cellulose*, p. 619. A silky, white cellulose was obtained which was prone to become somewhat decomposed in the drying-oven. After



Knudsen's Specific Gravity Chamber.

three chlorinations the derived cellulose failed to give a reaction with phloroglucinol, but produced a dark tint when dissolved in strong sulphuric acid.

The samples were marked as below, the first representing the more dense wood. They were found to contain:

No. of Sample.	Per Cent of H ₂ O.	Per Cent of C ₆ H ₁₀ O ₅ .
I	8.21	60.0
II	8.22	59.5
III	9.19	61.0

The results are based on bonedry samples. As a comparison it may be mentioned that Renker found 60.55 percent of cellulose, while Dean and Tower in red spruce heartwood found 58.9 per cent. No conclusions can be drawn from these findings, as the variations in the cellulose content are small and probably well within the limits of accuracy of the involved process of manipulation. It was therefore attempted to digest larger quantities of the same samples. Three leaden containers, each holding about one pound of chips, were lowered into the same digester to insure a similar treatment. Sample II proved less amenable to bleaching, but the yields did not otherwise vary appreciably, running from 47 to 48 percent, and incidentally in the same order as before.

It was realized from the very beginning of these experiments that in order to achieve results, it would be necessary to make comparative tests based on similar volume and not on similar weight. The earlier developments only strengthened this supposition and

*From Paper.

¹M. Renker, Dissertation, Berlin, 1909.

²A. L. Dean and G. E. Tower, Journal of the American Chemical Society, 1907, p. 1,119.

finally a specific gravity determination of the various samples was successfully carried out.

A sketch of the apparatus used in these experiments is shown herewith. The apparatus consists of a box of varnished birchwood, the walls and bottom of which are 20 mm. and the cover 40 mm. thick, with inside dimensions 180 by 180 by 40 mm. In order to avoid airbubbles the cover is made with an even slant to form an area 50 by 50 mm., about 10 mm. above the bearing surface. An opening cut at right angles in the bottom of the box serves as outlet, three similar openings in the cover as inlets; all of these apertures are fitted out with glass tubes of 3 mm. bore. The box rests on a rack in order to be easily accessible.

When conducting an experiment the container is first nearly filled with mercury. The cover is then put in place and fastened with four clamps, and more mercury run in, until it shows in the inlet tubes, or about 10 to 15 mm. In this way the capacity of the apparatus is ascertained and always checked and re-determined for every test. Sufficient mercury is then drawn off through the outlet, the cover removed, a weighed disk placed in the container, the cover replaced and the apparatus refilled as before. Any mercury displaced is then measured in a narrow calibrated tube. Two or more tests are run on each sample.

After it has been in use for a little while the capacity of the apparatus becomes perfectly constant. The use of washers is unnecessary, as the bearing-surfaces are placed to fit smoothly; this is very important, as a difference of only one-tenth millimeter in the compression would cause an error of 3.24 cc.

Results are tabulated as follows:

No. of Sample.	Weight Gm.	Moisture %	Cc. displaced mercury		Spec. gravity airdry.
			Run I.	Run II.	
I	209.6	9.6	427.3	427.5	0.49
II	124.9	10.1	274.8	275.0	0.454
I, II	114.0	9.9	293.6	293.6	0.388

As indicated in the table there is a maximal difference exceeding 20 percent and yet this does not represent the extreme limit of the possible fluctuation in the specific gravity, as the logs had been chosen rather indiscriminately. Each sample represented the species *Abies excelsa*, but from widely different localities.

For practical purposes the yield can only be determined by comparing the total output of a week's run. This was done again and again and always with the same result. When using chips from wood represented by sample No. I the average output of a digester was 9.66 tons, but when the mill was run with wood represented by Nos. II and III, the output was only 9.26 tons, which indicated that wood No. I was nearly 10 percent more valuable as a raw material.

The United States has long been the leading nation in the production of talc and soapstone, and its production of late is increasing. The output of talc for 1915 was 166,336 short tons, valued at \$1,401,197, and of soapstone 20,555 short tons, valued at \$490,385, according to J. S. Diller, of the U. S. Geological Survey.

RAPID NICKEL PLATING.*

By OLIVER P. WATTS.

During the greater part of the half century that nickel plating has been practiced, platers were content to follow in the footsteps of their forefathers and deposit nickel at the snail's pace of three to five amperes per square foot. A few years ago "rapid nickel salts," claimed to permit of nickeling at two to three times the usual rate, were imported from Europe. These proved to be only mixtures capable of yielding more concentrated solutions than that enemy of progress, the "double sulphate," which for so long has masqueraded as the plater's friend. The American plater soon learned how to make up his own rapid solution, and as a result nickeling at ten to twenty amperes per square foot is very common today.

The most recent step in rapid nickeling, if nickel's twin-brother and rival, cobalt, may be included in this category, is the remarkable work of Kalmus and Barrows¹ in plating with cobalt at 150 amperes per square foot, turning out commercial plating of high grade in three minutes.

These achievements with cobalt suggested the desirability of obtaining similar effects with the cheaper nickel solution. In so far as the wonderful results of cobalt solution XIII B depend upon its extreme concentration (312 grams of anhydrous cobalt sulphate, equivalent to 585 grams of the crystallized salt, per liter, or 7½ pounds per gallon) it should be possible to duplicate them with nickel, since its salts are equally soluble. It is in the matter of anode corrosion and in its absorption of hydrogen² that nickel is inferior to cobalt as a metal for electro-plating.

The nickel anode becomes "passive" on the slightest provocation and instead of all of the current dissolving nickel as is desired, a portion of it is spent in producing acid at the anode. Besides cutting down the efficiency of deposition, this acid causes hydrogen to be evolved in considerable quantity on the cathode, where some of it is absorbed by the deposit. Absorption of hydrogen by nickel renders it hard and brittle, and is likely to cause it to curl away from the metal on which it is deposited. The addition of a small amount of some chloride to the sulphate solution usually used for nickel plating is a well-known remedy for this passivity of the anode.

Previous experience with hot nickel solutions indicated their use for overcoming the difficulties just mentioned, since in a hot solution anode corrosion is greatly improved and absorption of hydrogen is lessened.

A 25-gallon (95 liter) hot nickel bath was used at 125 to 150 amperes per square foot (14 to 16 per sq. dm.), with great satisfaction, producing in five minutes a heavier deposit than is obtained in an hour from the usual "rapid" bath at ten amperes per square foot. In

*Paper presented at the 29th General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

¹Trans. Am. Electrochemical Society (1915), 27, 75.

²Idem. (1915), 27, 121.

spite of the extreme current density the deposits were superior in quality and adherence to ordinary nickel plate. Since the electrical instruments and current supply were inadequate for working this bath to its full capacity, a portion was removed to an enameled pail where it could be tested on small cathodes.

This solution contains nickel sulphate (single salt), nickel chloride, and boric acid in the following proportions:

	Grams/Liter.	Oz./Gallon.
NiSO ₄ ·7H ₂ O	240	32
NiCl ₂ ·6H ₂ O	20	3
H ₂ BO ₃	20	3

At the outset the anodes were the same that have been used in the plating laboratory for a number of years, viz., strips of electrolytic nickel. Later cast anodes of the same material were employed. Results of some of these tests are presented in Table I:

TABLE I.

Exp.	Temperature		Time	Amperes per		Amperes per		Deposit.
	C.	F.		Sq. Dm.	Sq. Ft.	Sq. Ft.	Sq. Ft.	
No. 10	67	153	5	31.7	295	24.5		Fine
No. 48	71	160	5	47.6	422	28		Good
No. 54	92	198	1	95.3	890	14.8		Fine
No. 4	25	77	3	5.3	49	3		Fine
No. 5	25	77	6	14	130	0.5	Mat. polishes well.	

In no case was the deposit "burned." In No. 5 there was a vigorous evolution of gas, indicating a low current efficiency of deposition. Deposits from the hot solution were mat, but polished easily.

It is a matter of general observation that electrolytic deposits become rougher with increasing thickness; when comparing different plating baths it is therefore desirable to know the thickness of the deposits as well as their physical qualities. For the same current efficiency, the thickness of nickel deposited will be proportional to the ampere-hours per unit of surface. By a comparison of the ampere-hours per square foot in the accompanying tables, the relative thickness of different deposits may be estimated. At 100 per cent efficiency one ampere-hour per square decimeter deposits 0.0123 mm., and 10 ampere-hours per square foot deposits 0.00052 inches, or 0.001 inch in thickness requires 19.2 ampere-hours. One hour at 10 amperes per square foot, or 10 ampere-hours, is considered good nickeling, and a common cobalt deposit by Barrows was 150 amperes per square foot for three minutes, or 7.5 ampere-hours. Judged by these standards the results shown in the tables are heavy deposits.

In order to secure samples from hot and cold solutions for direct comparison polished aluminum cathodes were used, for which the nickel was easily stripped.

DEPOSITS ON ALUMINUM.

Exp.	Temperature		Time	Amperes per		Amperes per		Deposit.
	C.	F.		Sq. Dm.	Sq. Ft.	Sq. Ft.	Sq. Ft.	
No. 12	74	165	20	18.9	176	60.3		Fine, mat.
No. 14	35	95	12	11.7	109	22.6		Rolled up, brittle.
No. 15	38	100	22	8.2	76	27.9		Mat, tore in buffing.
No. 49	71	160	5	24.2	225	18.7		Fine.
No. 50	78	172	10	30.7	285	47.6		Fine.
0.002 inch (0.05 mm.) thick.								
No. 53	98	208	25	15.2	141	60		Five successive deposits.

Plating on aluminum brought out the difference between deposits from cold and from hot solutions. An excellent deposit was obtained from the hot solution in every case, which bore polishing without peeling from the aluminum, and when stripped from the latter proved of excellent physical quality. Most of the deposits from the cold solution rolled up and partly separated from the cathode while in the plating bath, and in the few cases where this did not happen the deposit was torn during polishing. No. 53 consisted of five successive deposits for five minutes, each coating being polished and immersed in the electric cleaner for ten seconds before re-plating. It is 0.0025 inch (0.06 mm.) thick, and is harder than the usual deposit from a hot solution.

Current efficiency tests were made by reading the current on a Weston model No. 280 ammeter, and determining the weight of metal deposited in five or six minutes. Since a difference of three seconds changes the weight of a five minute deposit by one per cent, the results are subject to an error of at least this magnitude. Current efficiencies above 90 per cent are obtained in the hot solution at 20 amperes per square decimeter (190 amp. sq. ft.). It is evident from the tests that heating the solution and lowering the current density raises the current efficiency.

CURRENT EFFICIENCY TESTS.

Exp.	Temperature		Time	Amperes per		Amperes per		Cathode Eff.
	C.	F.		Sq. Dm.	Sq. Ft.	Sq. Ft.	Per Cent.	
No. 11	45	113	6	31.1	289	28.9		89.6
No. 13	29-40	84-104	6	31.1	289	28.9		19.4
No. 16	60-70	140-158	13	8.6	80	17.3		100.9
No. 46	25-28	77-82	5	19.4	180	15		31.7
No. 48	91-84	196-183	5	9.5	88	7.4		98
No. 51	77-73	171-163	6	26.4	245	24.5		100.5
No. 52	76-84	167-183	6	51.3	477	47.7		99.2

Polarization at the end of No. 52 was only 0.16 volt. Measurements of polarization at 70° C. (158° F.) gave 0.15 volt at current densities varying between 13 and 26 amperes per square decimeter (121-242 amp. sq. ft.). It is therefore probable that hot nickel solutions can be operated at high current densities with less anode surface than is at present used for current densities of 10 amperes per square foot.

In experiments with a solution containing 75 grams per liter (10 oz. per gallon) of the "double sulphate" two and a half times the current was required to cause burning at 70° C. (158° F.) that produced this effect in a cold solution, the weight of metal deposited being the same in the two cases. This indicates that concentration of metal is a greater factor in permitting the extremely high current densities used in these hot solutions than is the temperature. The beneficial effect of heating a nickel solution consists in the improved quality of the deposit, and in better anode corrosion. To avoid convection currents the flame by which the solution was heated was removed at the beginning of each test. At the higher current densities there is noticeable heating of the solution by the current.

A nickel solution that is extensively used consists of the single sulphate, boric acid, and common salt. In

order to learn if the substitution of common salt for the nickel chloride of the laboratory plating bath would cause any marked difference in its operation the following solution was tested:

	Grams/Liter.	Oz./Gallon.
Single sulphate	240	32
Sodium chloride	30	4
Boric acid	22	3

TESTS OF BATH WITH SODIUM CHLORIDE.

Exp.	Temperature, C°	Temperature, F°	Time, Min.	Sq. Amperes per Dm.	Sq. Amperes per Ft.	Amperes-Hours per Sq. Ft.	Per Cathode Eff. Cent.	Deposit.
No. 42	32	90	5	19	177	14.7	55.6	Good.
No. 43	71	160	5	19.6	184	15.3	82.3	Burned one edge.
No. 44	76	169	5	20.8	193	16.1	82.8	Burned one edge.
No. 86c	84	183	3	20.2	187	9.3	...	Fine.
No. 68d	78	172	4	25.3	234	15.6	...	Burned.

Although this solution gave fine results, it is inferior to the bath containing nickel chloride, in not permitting the use of so high a current density.

To make up the bath with nickel chloride proceed as follows: Dissolve the nickel salts in the proper amount of hot water, add nickel carbonate in small amounts at a time and heat until all acid is neutralized; either filter or allow to settle and decant the clear solution, and finally add the boric acid.

In so far as anode corrosion is concerned, any soluble chloride might be substituted for the nickel chloride, but not without some effect on the character of the deposit. Magnesium chloride or sodium chloride seems to be preferred for this purpose. In case either of these is used, neutralizing might well be done by the carbonate of the same metal. Ammonium salts and the "double sulphate" of nickel are to be avoided, since they are likely to cause crystallization from the solution when cold.

To obtain the best results from a hot solution the current density must be high; cables and tank rods must therefore be of ample capacity. Control of a hot solution by regulation of the amount of anode surface will probably be easier than in a cold bath. The heating coil should be of heavy lead (or hard lead) pipe, with a settling space of five or six inches below the lowest coil; lead will also serve as a lining for the tank. If an electric cleaner is operated from the plating dynamo, either the heating coil should be electrically insulated, or all rheostats should be connected on the cathode side of the line. Should gas pitting occur on first using the solution in the morning, it may be avoided by heating the bath to boiling for a few minutes before beginning plating. Seventy degrees centigrade (158° F.) is a good temperature at which to operate a hot nickel bath.

Owing to the peculiar properties of electrolytic nickel, the advantages of a hot over a cold solution are greater in nickel plating than in the deposition of any other metal.

ADVANTAGES OF A HOT OVER A COLD NICKEL SOLUTION.

1. Heating from 25° to 70° C. (79° to 158° F.) lessens the resistance of the solution one-half.

2. The current density may be increased two and a half to three fold.

3. The current efficiency, if less than 100 per cent in the cold solution, is raised.

4. Anode corrosion is greatly improved, and higher current densities may be used at the anode as well as at the cathode.

5. The deposit is superior to ordinary nickel plate in toughness and freedom from peeling.

6. In the solution tested, plating may be done at 200 to 300 amperes per square foot (22 to 33 per sq. dm.), at which rate the same amount of metal is deposited in five minutes as requires one and a half hours in the "rapid solutions" row in use at ten amperes per square foot.

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A PRACTICAL DESIGN FOR A TUNGSTEN OR MOLYBDENUM-WOUND FURNACE.*

By F. A. FAHRENWALD.†

The design of furnace herein described is that worked out for use in a series of experiments which required long-time runs at high and constant temperature.

Fig. 1 is a vertical section showing the wire-wound inner tube *A*, the annular winding space *B*, and the

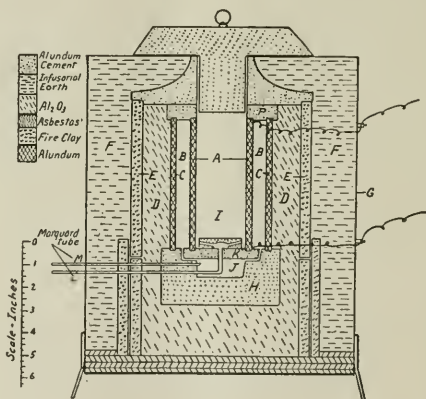


Fig. 1.

second concentric tube *C*. These tubes were of a very dense alundum, and were quite impervious to gases. The space *D* was filled with pure, finely ground Al_2O_3 held in place by the fire-clay cylinder *E*. The annular space *F* was filled with infusorial earth, and the whole contained within the sheet iron jacket *G*. The bottom was protected with several layers of $\frac{1}{4}$ in. asbestos board, on which the fire-clay cylinder containing the alumina-packed heating unit was placed. The unit *H* served as a base for the two inner alundum cylinders.

*From The Journal of Industrial and Engineering Chemistry.

†Case School of Applied Science, Cleveland, O.

and into this were cemented two Marquard tubes, one of which (*L*) carried the required atmosphere to the melting chamber *I*; while the other (*M*) opened through *J* into the winding chamber *B*.

Fig. II shows the manner in which this gas distribution was accomplished. The parts here shown were moulded from alundum cement and when dry were carved to proper shape, and then burned. The larger unit *H* was so constructed that when the disc *A* was cemented into place over the depression *J* shown in *H* a practically gas-tight chamber was formed connecting gas tube *M* to the openings *N*, which led to the wind-



Fig. 2.



Fig. 3.



Fig. 4.

ing chamber. The tube *L* connected opening *O* with the crucible chamber.

Fig. III shows the inner tube *A*, with winding of spring coiled wire (which was wound more closely near the end of the tube) in position on its alundum base. The winding here shown was of 10.0 mil tungsten wire, but it was found subsequently that there was less danger of fracturing the heating element if several wires were stranded and then wrapped around the tube without coiling. Before placing in the furnace, a heavy coat of alundum cement was added to keep the wire in position. For this work the smooth tubes seem to possess a less tendency to crack than do those made with the spiral groove.

Fig. IV shows the exterior of the completed furnace with gas tubes projecting. These tubes are connected directly by rubber hose to the gas supply. Electrical connection was made by twisting several wires onto the ends of the heating coil and carrying them through the insulating materials to binding posts on the outside (on the far side of the furnace in Fig. IV).

This furnace could be raised to 1500° C. in about 45 min. and held at that point on a wattage of approximately 800; hence, if the drop of potential across the furnace was 100 volts, 8 amperes would be required. The constancy of temperature depended almost entirely upon the regulation of gas flow. The insulation was so efficient that when the heating chamber registered 1500° C. the outer jacket was at about 80° C. This furnace was run up to 1800° C. and in one experiment it was maintained at a temperature of 1500° C. for six days with no variation that could be detected with an optical pyrometer.

PRODUCTION AND FOREIGN TRADE IN TANNING EXTRACTS.

Census figures just issued show a gratifying increase in the production of tanning extracts in the United States between 1909 and 1914. This increase was accompanied by a falling off in imports and a large increase in exports.

From 1909 to 1914 the yearly American production of chestnut and oak extracts increased from 234,066,555 pounds to 320,838,788 pounds, or by 37.1 per cent; and of hemlock extract, from 12,588,078 pounds to

17,579,866 pounds, or by 39.7 per cent. The increase in values of these products, however, was less marked. The value of chestnut and oak extracts increased during the five-year period from \$3,603,629 to \$4,044,477, or by 12.2 per cent, while that of hemlock extract increased from \$280,487 to \$312,317, or by 11.3 per cent. The value of other American manufactured tanning extracts and materials (for which no figures as to quantity are given) declined during the same period from \$3,881,116 to \$3,301,233, or by 14.9 per cent. The value of the entire group increased from \$7,097,680 to \$7,658,027, or by 7.9 per cent.

By far the larger portion of our imported tanning extracts is derived from quebracho, which supplied 120,450,283 pounds in the fiscal year ended June 30, 1915, as against 6,191,232 pounds for extracts derived from hemlock and other woods. There was a downward tendency in imports of extract of quebracho from 1909 up to the close of the fiscal year 1914, the total decreasing in that period from 102,004,981 pounds to 93,329,087 pounds, or by 8.5 per cent, while the value declined from \$2,740,530 to \$2,543,302, or by 7.2 per cent. The unusual activity in our domestic leather industry during recent months, however, has resulted in the high-record total of 120,450,283 pounds, valued at \$3,676,749, in the fiscal year 1915, above referred to.

Along with this falling off in imports, however, there occurred a very decided increase in exports, although the amount of tanning extracts sold abroad is still but a small fraction of the total American output.

NEW FORM OF COLOR-MATCHING LAMP.*

By McFARLAN MOORE,†

Elaborate spectrophotometric investigations have been made to proving that all articles when viewed solely by the light of the tube lamp have exactly the same shades of color as they possess when viewed by the light of a clear sky. It is stated that all dyers and other color experts agree that the standard light which they wish for color judging is that entering a window from a clear north sky at an angle of about 45° and preferably about mid-afternoon with a clear sun shining in the southwest.

The spectrophotometric curve of carbon-dioxide gas consists of a broken line with many jagged peaks, but an average of these peaks results in a smooth curve which gives a correct idea of the effective color characteristics so that it should be used to compare with the spectra of other sources. The effect of the banded character of the CO₂ spectrum, the tabulation of which consists of a broken line, was thoroughly investigated to determine its relation to the color-matching properties of the lamp.

The following samples of colored silk, taken from the National Color Card of America, were selected to represent all parts of the spectrum, and were spectrophotometrically tested to determine what the actual color composition was: Violet, National blue, Yale blue, emerald, lemon, orange and scarlet.

The results of each of these tests were carefully plotted in the form of a curve, and a review of the data obtained in connection with these reflection curves shows that the irregularities in the CO₂ spectrum are absolutely without visible effect, and that they deviate only very slightly from north-sky values to which they are compared. It has been pointed out that if these north-sky values had all been taken at an angle of about 45°, there would have been no detectable variation, and that therefore the color-matching values of the CO₂ spectrum were all that could be desired.

Fig. 1 shows an exterior view of this new color-matching unit. The straight tube lamp is contained in an elongated sheet-metal case, which is provided with a screw base similar to that used on the larger sizes of incandescent lamps. Instead of the lamp being fed CO₂ gas by means of an electromagnetic feed valve, it is generated automatically within the tube itself. Near each electrode is placed a small bulb about an inch long, containing calcium carbonate, from which emanates CO₂ gas when the resistance wires imbedded in it became heated to exactly the proper degree by reason of their being connected in shunt to the gas column. See Fig. 2. The gas column is 0.875 in. in diameter and 1 ft. long, and appears as a solid bar of light of intense whiteness. The foot-candles

available near the tube are over 200, thereby making this apparatus suitable for the very closest color discriminations. The degree of vacuum is automatically held within 0.001 of a millimeter, and the apparatus will stand wide line-voltage fluctuations without becoming disarranged in any way. The lamp takes about 240 watts.

Since light is the source of all color, it has been proposed that this new lamp receive official recognition from the International Conference on Electrical Units and Standards.

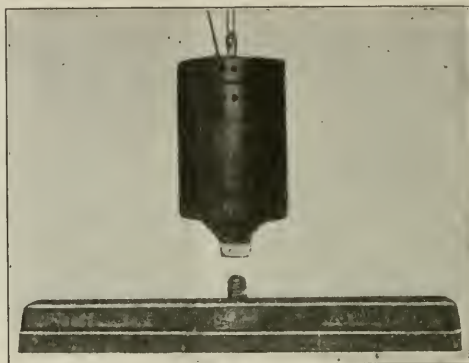


Fig. 1—Lamp with Transformer.

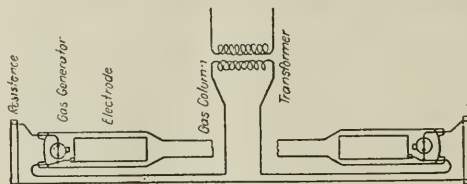


Fig. 2—Diagram of Connections.

This new lamp is suitable for making absolutely correct color determinations, and is applicable to a very wide field, but is particularly useful in enabling the dye shops of the great textile industry to run night shifts.

METALLURGICAL SMOKE.

With the idea of bringing about a better understanding between the metallurgical industry and agriculture as to the troublesome smoke problem at smelting and ore-roasting plants, the United States Bureau of Mines has issued Bulletin 84, "Metallurgical Smoke," by Charles H. Fulton, consulting metallurgist.

The bulletin is published primarily for persons who seek information on the subject of metallurgical smoke but are unacquainted with the technical language of metallurgy. It is, of course, not possible to free a technical subject entirely from technicalities, but, so far as possible, statements are made in plain and simple English.

*Condensation of paper read before the New York Section of the American Electrochemical Society, in joint session with the Illuminating Engineering Society, on Nov. 11, 1915.

†Edison Lamp Works, General Electric Co., Harrison, N. J.

SOME FAULTS OF THE SMALL ELECTRIC-ARC FURNACE FOR MELTING AND REFINING STEEL.*

By W. M. MCKNIGHT,†

The small electric arc furnace is rapidly coming into favor for the production of small, highly-refined steel castings, and its advent is welcomed by both the manufacturers of steel castings and the electric power companies. Without going into the merits of the electric furnace as a competitor of the crucible furnace and open-hearth furnace, regarding the quality of the product or regarding it as a welcome load builder for power companies, I wish to point out some of the handicaps to its universal adoption and successful operation.

Process.—The furnaces that are now in operation in several parts of this country, while differing in some respects in their mechanical construction and electrical demands, all refine the steel by the same chemical process; *viz.*, by raising the temperature of the bath to 2,500° C. or better, by boiling the metal to eliminate the impurities, and by the introduction of the necessary refining agents to bring it up to the fineness desired.

Construction.—All small arc furnaces are constructed on certain general mechanical lines, as follows: The furnace consists of a steel shell mounted on trunnions for tilting to discharge the molten metal. This jacket is lined with a highly refractory lining, sufficiently thick to retain the heat; the lining and shell, however, are pierced with port-holes for the purpose of charging the furnace with steel, adding the refining agents, discharging the refined metal and for inserting the electrodes, and all these port-holes furnish avenues of escape for the heated gases. The electrodes are secured in place by the holders mounted on the tilting shell, and the holder raises or lowers the electrode by hand operation, by hydraulic control, or by electric motor control.

Efficiency.—In spite of the fact that the electric furnace, today, is turning out small castings of a better quality and at a lower cost than by other processes, nevertheless, the over-all efficiency of the best furnaces on the market is far from 100 per cent.

There are three principal sources of loss:

Electrical: In the improper delivery of the energy to the metal.

Mechanical: In the improper design of the furnace shell and ports, to exclude cold air and retain the heat.

Chemical: The improper combinations of refractory materials, that should be inexpensive in first cost, withstand the intense heat long enough to avoid delays through the interruption of the manufacturing process, and not introduce any chemical combination with the metal. Also, there should be found an electrode that will not waste away too rapidly through

oxidation, within and without the furnace, as it comes in contact with the air and gases.

Electrical conditions can be improved by supplying the proper current at the proper potential. Mechanical conditions can be improved by re-designing detail portions of the furnace. The chemical conditions can be improved only by exhaustive research and careful study.

Refractories.—Refractories are of two kinds: the heat-resisting linings and the heat-producing electrodes. The heat-resisting linings may be either acid or basic, depending on the degree of heat required for the quality of steel to be turned out. The heat-producing refractories may be either carbon or graphite.

Temperatures.—Merely to melt down steel scrap and turn out castings of semi-steel and low-grade castings of unknown quality does not require a temperature of 2,500° C., and for a furnace for this class of work an acid lining of silica is successfully used. To refine the steel, however, it is necessary to use a basic lining of magnesite, at least where it comes in contact with the bath, or where the heat would be intense enough to melt down the silica and cause it to run down into the bath and combine with the metal bath or slag and the basic lining, thereby changing their character.

Lining.—The furnace linings can be put in in two ways: build up with brick work, the bricks made to conform to the shape of the shell and laid up in a basic paste or coal tar binder, or the material for the lining may be made up into a mass and rammed into the shell. The brick lining offers some advantages, inasmuch as it has passed through a glazing process that should prolong its heat-resisting qualities, but it is expensive, particularly if special sizes and shapes are desired, and if the source of supply is remote, and the delivery uncertain.

The rammed lining should be superior from the fact that it is, if properly put in, a monolithic mass, hence there should be little danger of the bath breaking through to the shell, with the resulting damage to the furnace and loss of the bath.

Electrodes.—Electrodes are of two kinds: carbon and graphite. Each has its merits. The carbon electrode is the less costly, but has less electrical carrying capacity than graphite, and consequently must be greater in cross-section to deliver the same amount of energy. It therefore has a larger amount of radiating surface, and consequently the saving in first cost of the carbon is offset by the loss in energy dissipated in heat. Owing to the intense heat of the electrode, its surface both within and without the furnace shell loses carbon by its surface contact with the air and resulting oxidation.

The graphite electrode, by virtue of its greater carrying capacity, is smaller in diameter, and offers less surface for radiation of heat and oxidation. The electrode within the furnace shell is subject to further attack by the passage of the electric current through

*Paper presented at the 29th general meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

†Southern California Edison Co., Redondo Beach, Calif.

the heated gases to the lining, which, at a temperature of $2,500^{\circ}\text{C}$., itself becomes a very good conductor of electricity.

CONCLUSIONS.

Electric steel castings may not be better in quality than those turned out by skilled operators with fuel furnaces, but small electric steel castings can be made at a less cost under present conditions, which conditions could be improved, and then the furnaces will be limited only by the capacity of the source of the supply of electrical energy.

The field has apparently no limitations, if the chemist can overcome the losses I have pointed out. Formulate a better refractory lining, an electrode that will not waste away except in heating the bath, and utilize the waste gases by manufacturing them into a by-product or by-products.

I have only touched on one single product which gives promise of so much for the electric furnace. The field is undeveloped and has almost unlimited possibilities. In three Pacific Coast States alone, I am informed, there is approximately 1,000,000 H. P. in water-power going to waste, because a too zealous government is retarding its development, by capital ready and willing to invest, if more liberal terms of lease can be secured. Such terms might be forthcoming if the American Electrochemical Society would bend its energies to make efficient power consuming devices.

This certainly is the day for the chemist, and his greatest achievements will be in the electrochemical field.

METHOD FOR REMOVING HAIR FROM HIDES.

Since the war sodium and arsenic sulphides, which are largely used in the unhairing of hides, have reached almost prohibitive prices. In a paper read before the Yorkshire section of the Society of Chemical Industry, Mr. J. E. Pickles, of the leather department of the University of Leeds, described how experiments at the university have shown that a substitute is to be found by boiling lime with sulphur, and then adding soda in the calculated amounts to give the same effects as sodium sulphide. The sulphur was added to the lime without slaking, and, if necessary, boiled with the lime until all the sulphur was dissolved. This gave a yellow-colored liquid. The soda could be added during or after slaking. This lime had been used in the experimental tannery of the university, and two packs of calf skins for chrome tanning were ready for unhairing in four days, and as far as could be seen there was no difference between these skins and those unhairing with sodium sulphide. In the case of a pack of hides for chrome sole leather, more soda was added to the lime in order to increase the swelling, and these hides also were unhairing in four days. It had also been used for skins intended for vegetable tanned dressing leathers with equally good results.

DISTILLATION OF SANDALWOOD OIL IN INDIA.

An experimental factory now in course of erection at Bangalore, Mysore, for the extraction of sandalwood oil, will constitute practically a new industry for that native state. This oil has been manufactured in India from time immemorial, but the methods to be pursued at Bangalore are entirely different from current Indian practice. The following notes regarding this new factory are taken from a statement of the Director of Industries and Commerce in Mysore, in the Mysore Economic Journal:

The disposal of sandalwood in Mysore is a state monopoly which in recent years has produced a large net revenue. In 1913-14 this revenue amounted to 19.87 lakhs of rupees (\$644,650), produced by the sale of 1,862 tons of wood. The wood is mainly disposed of by auction sales held in November and December, but after the outbreak of war there was an almost complete cessation of the demand from European buyers. Latterly the business has revived, and at the auction sales at the end of last year good prices were obtainable for a fairly large quantity of wood. It is only the heartwood of the tree that is of great commercial value. In a small way it is used for carving; but the high prices that the wood brings are due to the fact that it yields an oil that is much used for medicinal purposes and in the preparation of perfumery.

The extraction of the oil from sandalwood is not permitted to private persons in the Mysore state, but the industry is to some extent carried on in districts adjacent thereto. The oil is also largely manufactured at Kanauj, in the Punjab, where it is chiefly used in the preparation of sweet-scented essences. So long as the state was enjoying a steadily increasing revenue from its sandalwood monopoly it was obviously undesirable to disturb the existing arrangements, but when the market for the wood collapsed at the end of 1914 it became necessary to consider what steps should be taken to preserve this valuable source of revenue.

The users of sandalwood oil in Europe and America either distill their own oil or purchase it from chemical firms of repute. Oil of Indian manufacture is unsalable because of defective distillation methods and the tendency to adulterate it with cheap oils. Very little was known about the methods of distillation employed in the west, and as a preliminary to any proposals to set up sandalwood distillation in Mysore it was decided to have the whole question thoroughly investigated, and this work was intrusted to Prof. Sudborough and Dr. Watson, of the Indian Institute of Science.

During the whole of last year and up to the present time the matter has been under investigation, and the results obtained are of a sufficiently satisfactory character to warrant the establishment of a factory where

the oil will be manufactured on a commercial scale. In the course of the experimental work a considerable quantity of sandalwood oil has been produced, the bulk of which has been sold locally at very favorable prices; and the oil which has been sent to England has been declared equal to the best that can be obtained in Europe and has realized equal prices. To pass the test to which the oil is subjected in Europe complete chemical control is necessary, and every consignment of oil sent out from the factory will be subjected to an examination, and a certificate as to its quality will be issued. In this way it is hoped to overcome the prejudice against sandalwood oil manufactured in India.

The auction sales of the wood will continue, and the new factory will purchase its supplies from the Forest Department at the same prices paid by outsiders. If the industry proves profitable, it is under contemplation to establish a distribution plant of sufficient size to deal with the whole annual output of sandalwood in the South of India.

AMERICAN CLAY IN PAPER MAKING.

Several interesting facts regarding the possibility of using American clays in the manufacture of paper were brought out at a recent conference between representatives of clay-mining companies and of the United States Bureau of Standards, which had been arranged for the purpose of discussing the status of imported and domestic clays in this industry. It was shown that several mills in this country were using American clays with excellent results, while several others making the same grade of paper had never been able to use anything except imported clays.

The facts indicate that part at least of the criticism of domestic clays is due to prejudice in favor of the imported article. Foreign clays are said to have a much whiter appearance than the domestic, yet it is definitely known that many imported clays are treated with ultramarine blue, giving them an artificial effect.

Representatives of the clay companies offered to supply all the American clays that would be needed by the Bureau of Standards in its investigation, and also offered the assistance of any of their representatives and their fullest co-operation in general. Several lots of the products of their largest mines are to be sent to the bureau. Samples of the best English products will be obtained for comparison.

It is proposed to make runs on the paper machine to determine the difference in rate and amount of settling-out of the clays, and to make tests for color, per cent of grit, ease with which the clays mix with water, and other experiments which will be devised to determine such characteristics as have a bearing on the problem.

PEPTONE AS AN ADDITION AGENT IN STANNOUS AMMONIUM OXALATE BATHS.*

By FRANK C. MATHERS and BARRETT W. COCKRUM.

The statement was made in the previous paper¹ that the best tin deposit was obtained from a stannous ammonium oxalate bath containing peptone as an addition agent, the use of which was discovered in this laboratory. Without the peptone the deposit is of no value as a protecting coat, because it consists of projecting needle-like crystals.

The effect of the peptone (Witte's) was remarkable. As soon as it was added, the tendency to form the projecting, loosely adhering crystals ceased and the deposit became so smooth and finely crystalline that thick cathodes (0.5 to 1 cm. thick) could be prepared, and so firm and coherent that shavings of tin could be cut from the deposit with a knife.

Clove oil, glue, gelatine and formin, agents which have been found effective with other metals, were practically without any beneficial influence in preventing the formation of the crystals. Licorice extract and aloes residue² prevented the formation of loose crystals but produced club-like projections formed on the cathodes.

Carbon disulphide, even in small amounts, made the deposit spongy and non-adherent, a condition which persisted until the carbon disulphide was exhausted, when the deposit again became crystalline. There was no intermediate time when a non-crystalline, solid deposit was obtained. The carbon disulphide was different from the other addition agents, none of which produced a spongy deposit.

Manipulation—The experiments were conducted as described in the previous paper.¹ The active area of the anodes was 32 sq. cm. and of the cathode 50 sq. cm. The volume of the bath was 300 cc. A current density of 0.4 amp. per sq. dec. (3.6 amp. per sq. ft.) was used. The anodes were amalgamated, to keep the anode slime out of the bath. The baths were stirred occasionally. Impurities in the anodes sometimes caused the formation of an insoluble coating which had to be removed mechanically.

Concentration of the Baths.—The addition of 0.1 to 0.5 per cent peptone to the bath containing 2.5 per cent stannous chloride, 5.5 per cent ammonium oxalate and 0.3 per cent oxalic acid (the composition generally recommended) gave a smooth, firm deposit on the bottom of the cathode but the top part was dark, clearly showing that the bath did not contain enough tin. Solutions materially more concentrated than the above formed crystals of a salt in the bath, a trouble which was greatly lessened by starting with stannous

*Paper presented at the 29th general meeting of the American Electrochemical Society held in Washington, D. C., April 27-29, 1916.

¹Mathers and Cockrum: Tests of Tin-plating Baths. Trans. Am. Electrochem. Soc., 29, — (1916).

²Trans. Am. Electrochem. Soc., 27, 131 (1915).

oxalate in place of the stannous chloride, whereby the ammonium chloride was eliminated.

The result of numerous experiments showed that a very satisfactory concentration and composition was 5 per cent stannous oxalate, 6 per cent ammonium oxalate, 1.5 per cent oxalic acid and 0.25 per cent peptone, as compared with 2.28 per cent stannous oxalate, 4.14 per cent ammonium oxalate and 0.3 per cent oxalic acid for the original bath.³ The principal advantage in using the increased amount of oxalic acid is that it prevents the "crawling of the solution up the sides of the beaker, owing to the capillary action of porous crystalline salts. Larger amounts of oxalic acid, 7 to 10 per cent, caused the formation of hard crystals of a stannous salt upon the electrodes. Acetic acid may be used in place of the oxalic, but it showed no advantage. A higher concentration, 7.5 per cent stannous oxalate and 9 per cent ammonium oxalate, caused more trouble from "crawling" and from the formation of crystals of salt. More ammonium oxalate than is required to dissolve the stannous oxalate and to keep the anodes clean is not desirable, because it greatly promotes the formation of salt crystals in the bath. Variation in the quantity of peptone was without much effect, but 0.1 per cent gave a rougher deposit than 0.25 per cent, the quantity which is recommended.

Maintenance of the Bath.—Continuous electrolysis of the bath produces a decrease in the concentration of tin, free oxalic acid and peptone. This decrease in the concentration of tin shows itself after a time by the darkening of the deposit, which finally becomes black and non-adherent and, at last, gas is evolved from the cathode. The addition of stannous oxalate immediately causes the deposit to become bright and coherent again, thus clearly showing that the trouble was caused by lack of tin.

The anodes, if they have become covered with a coating of insoluble material, must be washed with a brush until the pure tin is again exposed, and more ammonium oxalate should be added to the bath.

During electrolysis, a fine yellow precipitate forms in the bath and settles to the bottom as long as sufficient oxalic acid is present, but if the bath needs more oxalic acid, porous crystalline salts form on the sides of the beaker and on the electrode connections at the surface of the liquid, and gradually climb upward. The addition of more oxalic acid stops this.

More peptone must be added whenever the deposit shows projecting crystals.

Baths run at 50° C. (122° F.) required more doctoring than those at room temperature and the crystalline structure of the deposits was more pronounced.

In spite of these additions to the baths, they finally became so deteriorated that bright solid deposits could no longer be obtained.

Current Density.—A good deposit was obtained at 0.8 amp. per sq. dec. (7.4 amp. per sq. ft.). However,

the experiments described in this paper were run at half that density. The voltage averaged about 0.5 with the cathode midway between the two anodes, which were 4 cm. apart.

Other Salts in the Baths.—Potassium stannous oxalate is less soluble than ammonium stannous oxalate, hence potassium oxalate cannot be used in place of the ammonium oxalate. Potassium and ammonium chlorides were not desirable additions, on account of their tendency to form crystalline salts.

Character of the Deposits.—Some of the cathodes, when heated just a little above the melting point of tin, swelled and foamed, and the vapor which was given off burned, thus showing the occlusion of considerable amount of organic material. A porous, foam-like mass of metal remained if the heating was discontinued at the proper time.

CONCLUSIONS.

The addition of peptone to the stannous ammonium oxalate bath is essential for the production of a thick, smooth, finely crystalline deposit of tin. No other tin bath (except possibly the sulphide, which was not tried) is known from which such a thick, smooth deposit can be obtained.

A good composition of bath is: 5 per cent stannous oxalate, 6 per cent ammonium oxalate, 1.5 per cent oxalic acid and 0.25 per cent peptone. The stannous oxalate may be easily made by precipitating a solution of stannous chloride with oxalic acid.

The bath was run at room temperature at 0.4 amp. per sq. dec. (3.6 per sq. ft.). The solution must be stirred at intervals.

The authors wish to thank the American Electrochemical Society and its Committee on Assisted Research for the grant of money for the purchase of a portion of the materials used in this research.

ANOTHER SCHOLARSHIP IN CHEMICAL ENGINEERING.

The Chemists' Club of New York announce the establishment of another scholarship fund, the income from which, approximately \$400 per year, is to be devoted to assisting financially deserving young men to obtain education in the field of industrial chemistry or chemical engineering. This scholarship has been endowed by Mr. Wm. F. Hoffmann. Its benefits will be open to properly qualified applicants without restriction as to residence, and may be effective at any institution in the United States which may be designated or approved by the Chemists' Club. In accordance with the deed of trust applicants must, as a minimum qualification, have completed a satisfactory high school training involving substantial work in elementary chemistry, physics and mathematics and present a certificate showing that they have passed the entrance examination requirements of the college entrance examination board or its equivalent.

³Bath 1 of Kern's Report. Trans. Am. Electrochemical Soc., 23, 199 (1913).

The CHEMICAL ENGINEER

PUBLISHED MONTHLY by the MYRON C. CLARK
PUBLISHING CO.,

608 S. Dearborn Street, Chicago

*Entered as Second Class Matter, Aug. 19, 1907, at the Post Office
at Chicago, Illinois, under Act of March 3, 1879.*

Subscription—United States, Cuba and Mexico.....\$2.00
Extra postage to Canada 25c a year; to foreign countries 50c a year.
Remittances may be made by check, draft or money order in favor of
THE CHEMICAL ENGINEER

All communications should be sent to THE CHEMICAL ENGINEER, 608
S. Dearborn Street, Chicago, Ill.

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NOTES AND COMMENTS.

Potash in Lake Muds of Western Utah.

Potash in large proportions is present in the brines and muds of the Salduro Marsh, a sink in the Salt Lake Desert, about 60 miles west of the southwest edge of Great Salt Lake. From the clays underlying the salt body which covers the marsh the United States Geological Survey collected samples at depths of 8 to 12 feet, in which the dissolved salts were found to contain from 2 to about $3\frac{1}{2}$ per cent of potash, and $2\frac{1}{4}$ per cent was found in the soluble salts at a depth of about 4 feet. According to analyses made by the Survey, the brines and muds from the Salduro Marsh contain considerable magnesium chloride as well as chlorides of potassium and sodium, and so are somewhat similar in composition to the deposits from which potash is manufactured in Germany.

Census of Paper and Wood-Pulp Manufacture.

An increase of 24.1 per cent in the total value of the paper and wood-pulp production in this country between 1909 and 1914 is reported by the United

States Bureau of the Census, notwithstanding the fact that in the same period the number of establishments in that industry in the United States decreased from 777 to 718. Besides the concerns primarily interested in paper and wood pulp, reports were also received from nine establishments in 1914 and fifteen in 1909 which were engaged primarily in the manufacture of other products, such as paper boxes and roofing material, and produced paper only as an intermediate or subsidiary product. The production of wood pulp in 1914 amounted to 2,894,650 tons, as compared with 2,498,955 tons in 1909, the increase being 15.8 per cent. In addition to the domestic production there were used 534,395 tons of imported pulp in 1914 and 301,392 tons in 1909, the increase for this item being 77.3 per cent. The total value of the paper produced in 1914 was \$294,355,875, as compared with \$235,242,437 in 1909, the increase being 25.1 per cent.

Manufacture of Leather in United States.

According to the preliminary statement by the United States Bureau of the Census showing the results of the 1914 study of the manufacture of leather in the United States, there was a decrease of 19.5 per cent in the number of establishments between 1909 and 1914, but an increase of 12.1 per cent in the value of the products. The number of hides and skins of all kinds tanned during 1914 represented a decrease of 5.3 per cent compared with 1909, and the number of cattle hides tanned showed an increase of 25 per cent in value and a decrease of 4.5 per cent in number. Reports were received from 767 establishments having a total output valued at \$374,512,939. In 1909 there were 953 establishments with a total value of products amounting to \$334,105,561. Of the total number of establishments reported in 1914, twenty-seven were engaged primarily in other industries, but made leather to the value of \$7,160,436, and used it in further manufacture. In 1909 there were thirty-four similar establishments, which made and consumed leather valued at \$6,095,106.

Mounting for Protecting Thermoelements.

A mounting for protecting laboratory thermoelements from damage by contamination or by mechanical strains has been developed at the Bureau of Standards, Department of Commerce, in connection with investigations of the expansion of substances on heating. Protective mountings with convenient heads for attaching the leads to the millivoltmeters that indicate the temperatures are common with industrial thermocouples; but the wires of the average couple to be seen in a physical or chemical laboratory are either entirely unprotected or else merely have portions adjacent to the junctions inserted in glass or porcelain tubes. The mounting regularly used in the expansion laboratory of the bureau not only affords adequate protection to the thermoelement, but also

adds greatly to the convenience of its use. Scientific Paper No. 276, entitled "Protected Thermoelements," discusses this subject and persons interested may obtain copies, free of charge, upon request to the Bureau of Standards, Washington, D. C.

Proposed British Prohibition of Lead Paints.

The enactment of a law prohibiting the importation, sale or use of any paint material containing more than 5 per cent of its dry weight of a soluble lead compound is the principal recommendation of the British departmental committee appointed to investigate the danger of the use of paints containing lead to the health of persons engaged in painting buildings. The committee was appointed January 20, 1911, and, after extensive investigations, issued its report on May 5, 1915, which, on account of its importance, has been reprinted in full as Bulletin 188 of the Bureau of Labor Statistics of the United States Department of Labor.

The Vegetable Dyes of India.

Since the outbreak of the war in Europe investigations have been carried on in India jointly by the Departments of Industries in Mysore and Madras with a view to determining to what extent the present shortage of synthetic dyes could be made good by reverting to the natural dyestuffs of vegetable origin that were formerly employed. The work has been carried out mainly in the laboratories of the Applied Chemistry Department of the Indian Institute of Science, and with Prof. Sudborough have been associated Dr. H. E. Watson and Dr. F. Marsden, the tinctorial expert of the Government of Madras.

Dr. Marsden's report has recently been submitted to his Government and is reproduced in the Indian Trade Journal for March 3. The materials dealt with in the investigation included chay root, nuna, ventlago bark, *Rubia cordifolia*, red sanders wood, sappan wood, cutch, divi-divi and other tannin materials, annatto, kapila, lac, and *Wrightia tinctoria* leaves. Concerning annatto, Dr. Marsden says:

The dye obtained from jabara seeds was tested upon bleached mercerized cotton, upon which it gives a pleasing rich orange shade. The method of dyeing is simple, consisting in working the yarn in a warm alkaline bath made by extracting the dye from the dried seeds with water and then adding a little carbonate of soda or potash. The dyeing is finished by giving a weak bath of acid and rinsing.

It is generally assumed that the shades given by annatto are not fast, but I find that the fastness properties are equal to those of many of the bright aniline dyes which have been so largely used here, and there is no reason why, if the shade is liked, the material should not find a more extended use upon silk and cotton materials, in which brightness of color is a consideration.

Potash Production in United States.

Potash salts were produced in the United States in 1915 to the value of \$342,000, according to the United States Geological Survey. Though this figure is of interest as showing a small beginning in the domestic potash industry, it becomes of little impor-

tance if the total needs of the country are considered, for it represents a quantity consumed in less than a week under normal conditions.

The imports of refined potash salts in 1915 were 76,141 long tons, or slightly more than 25 per cent of those in 1913, the latest normal year of importation. Imports of the potash fertilizers, kainite, manure salts, and double manure salts, amounted to 20,427 long tons, or about 3 per cent of those in 1913. Taking all the potash salts together, the imports in 1915 were about one-tenth of those under normal conditions.

In the Survey report on the subject, W. C. Phalen states that potash was recovered within the United States as a by-product from the manufacture of Portland cement at Riverside, Cal. By-product potash from this source has yielded a considerable revenue, owing to the abnormally high price for these salts, and in obtaining it two other purposes have been subserved—first, the saving of additional material to be controverted into cement, and second, the elimination of the dust nuisance. At Riverside a discharge of 100 tons of dust a day over the surrounding orange groves has been prevented.

Potassium sulphate from alunite was first placed on the market late in October, 1915, by the Mineral Products Corporation, at Marysville, Utah. The production has not been large so far, owing to the incidents connected with a pioneer enterprise of this character. Though certain foreign deposits of alunite have been worked for potash alum, this is the first recorded yield of potash salts as such from alunite. The product is of high grade.

The plant of the Potash Products Co., of Omaha, Neb., was established in the spring of 1915 at Holland, near Alliance, in the northwestern part of the state. During about half of the year the company obtained potash salts from the brine of an alkaline lake in this region.

In addition to the output from the above sources, potash was marketed in 1915 from kelp obtained along the Pacific coast.

Experimental work on the production of potash salts from different sources was active during the year, and in places this activity has been succeeded by the construction of plants. Operations are in progress at Searles Lake and at Keeler, on the shores of Owens Lake, Cal. It is reported that one company is erecting a plant near Great Salt Lake and that another will soon be started at the south end of the lake. The by-product bittorn at solar evaporation plants on San Francisco Bay has also received some attention.

Another plant has been planned for the extraction of potash salts and alumina from alunite at Marysville, Utah.

Manufacturers of Portland cement, having had their attention directed to a possible revenue from by-product potash, will not be slow in thoroughly investigating their raw material.

The Chemical Engineer

PUBLISHED MONTHLY

at 608 S. Dearborn Street, Chicago, Illinois

Vol. XXIII.

CHICAGO, JUNE, 1916.

No. 6.

THE WAR AND AMERICAN CHEMICAL INDUSTRY.*

By **RAYMOND F. BACON**.†

The year 1915 will always be a notable one in the history of chemical manufacture in the United States. For 50 years several branches of chemical industry had been peering half-formed through the mists of chemical and political economics. For several decades other branches of manufacture had been affected by malnutrition and had failed to grow in strength. However, the present European war has exerted a reconstructive action, and since the beginning of last year chemical industry has borne rule over our other manufacturing activities.

Indeed, the past year marked the commencement of a period of industrial transition, national in scope, and characterized by the serious endeavors of American enterprise and ingenuity to bridge the gap which has existed in the chemical industry of the United States as compared with that of Germany. In this stupendous undertaking, carried out so far with conspicuous success, the industrialists of today have not collected the materials for the structure, but they have designed it and have been active in the work of building. Although perhaps a weak bridge, and built upon shifting sands, it has provided at least a temporary channel of escape from European dominance, and it is constantly being reinforced and otherwise strengthened.

It has been indicated¹ that the measure of a country's appreciation of the value of chemistry in its material development and the extent to which it utilizes this science in its manufactures, generally measure quite accurately the industrial progress and prosperity of that country. Moreover, the quality and value of an industrial product are based upon the application of correct principles in its conception, preparation, and use, and the correct principles can result only from scientific research.² The wonderful headway made so far by our newer chemical industries has resulted largely from carefully organized research, but we are still far behind the pace which Germany

has started. We must therefore strive for a greater recognition of the national value of industrial research.

At the expense of the unfortunate warring countries, the manufacturers of the United States have played a most important part in the markets of the world in the last thirteen months, and all possible efforts are being made through individual enterprise and through various commercial organizations to deal adequately with the export situation. Not only has the war opened the gates of world-wide commerce to the United States, but it has provided a tariff wall that has allowed our nation to develop its industries along broad lines.

While almost every branch of American industry has been directly or indirectly affected by the European war, its influences have been particularly felt upon all branches of chemical industry. It has operated detrimentally to many lines of manufacture, but in the business connected with the furnishing of war supplies there has naturally been a great stimulus to trade.

Two great interests in the United States have been especially acted upon by the prevailing war. The total cessation of the shipment of potassium salts from Germany to this country has seriously disabled the American fertilizer industry; this handicap has, in fact, resulted in material injury to the agricultural sections using fertilizers, particularly the cotton belt of the South. Likewise the almost total stoppage of shipments of dyestuffs from the great German factories, which ensued with the opening of the war, over a year ago, has been seriously felt throughout the textile, paint, and other of our industries in which dyestuffs are consumed in large quantities.

As the result of international negotiations, there have been from time to time, some transatlantic movements of dyestuffs and potassium salts, mostly, it is understood, through neutral ports adjacent to Germany. The United States has secured a share of these commodities, but the importations of potash have been very limited indeed, when compared with the shipments of dyestuffs which have occasionally reached the American markets. It has also been possible to obtain supplies of certain needed dyes through Swiss manufacturers, in exchange for intermediates shipped from the United States to Switzerland. Then, too,

*Paper presented April 18 at Urbana, Ill., meeting of American Chemical Society.

†Director of the Mellon Institute of Industrial Research, Pittsburgh, Pa.

¹Bacon, Science, 40 (1914), 871-81.

²Bacon, Sci. Am. Suppl., 80 (1915), 334.

there have been importations of logwood and other vegetable dyestuffs from colonial possessions of several of the warring nations.

With such an acute situation confronting several of our leading industries, there has naturally been great activity to assist in meeting it, and especially to encourage the development of a domestic production of potash fertilizer material and dyestuffs within the nation; and material progress has been made in the production of dyes and chemicals from the increasing quantities of intermediates supplied from many new sources throughout the country. The present crisis has, in fact, evoked deep interest on the part of all concerned—tar distillers, manufacturers of chemicals, manufacturers of dyestuffs, the many users of dyes, and American economists. The producers of "by-product coke" have shown a gratifying readiness to multiply their recovery plants for the production of benzol and tar, and considerable capital and experience have been embarked in steps to build up a distinctly American coal-tar chemical industry.

The developments which have recently taken place in the manufacture of products formerly imported largely or entirely from Europe, are primarily instanced by the activity of those manufacturers who are interested in the industries discussed below.

American Coal Products.—Under prevailing abnormal conditions, quite a large number of small plants have been erected for the production of products derived from coal. On the whole, these are now being operated at a pleasing profit; but at the end of the war many of them will probably fall like autumn leaves. While it is true that some of them may struggle on and pawn their war-bridal gifts in a hopeless endeavor to establish permanent business, only those which have been constructed on a sound economic basis will be numbered among the eventual survivors.

It is well known to chemists that the manufacture of products derived from coal is not an industry *per se*. It is, in fact, based upon, or rather an extension of, the manufacture of certain halogens, mineral acids, and alkalis. It follows from this dependence that a permanent coal products chemical industry cannot be created in America except by co-operation with or enlargement of the American acid and alkali manufacturing companies. The full realization of this basic consideration insures the long life of several of the large American producers in this field. These companies seem to be fully cognizant of the fact that with prices ten to fifteen times normal, it is now possible to manufacture some coal products with large profit in this country, but that with the return to normal conditions all processes must be combined with strict attention to rigid scientific methods.

Experience shows that the coal products chemical industry is vital to national defense—the basis of modern warcraft and hence the real source of military strength. Munitions cannot be manufactured in sufficient quantities during the exchange of diplomatic

notes prior to the inception of hostilities; they must be produced and stored for future use long in advance of war. Under the aspect of our present international relations, none can doubt the propriety of increasing our means of defense. This can give no cause of offense nor increase the danger of a rupture. If on the other hand, our Government should fold its arms in security and at last be involved in war for the maintenance of its rights without adequate preparation, the responsibility would be of the gravest character. Should collision be avoided, as we all sincerely hope it may be, the expenditures in making the preparations will not be lost. One main national defense is that great coal products chemical plants be established and operated continuously at commercial profits during peace, in order that they will be immediately available to produce unlimited ammunition during times of war. The establishment of a complete and profitable coal products industry is essential for the success of any program of national preparedness.

Such an industry must, however, be founded and operated on a basis to keep abreast with scientific progress. The steps essential to this progress are as follows.² The manufacture of nitric acid from the air on a scale which will render the nation entirely independent of supplies of foreign nitrates; a reasonable tariff which will divide coal products into classes according to their degree of advancement in manufacture and will levy duties proportionate to this degree; and the provision of an anti-dumping clause, to prevent unfair competition instituted for the purpose of destroying American industry.

It seems to be assured that a great coal products industry will result from the present activity and interest, but the degree to which this industry attains perfection will be proportionate to the extent with which the fundamental requirements for its profitable operations are provided.

Benzol.—During the past 15 years the production of benzol has steadily increased in the United States. In fact, there was enough benzol at all times for the manufacture of dyes, if a coal products industry had been established by the assistance of the Federal Government and by the sustained support of the American textile industrialists. Not only were both of these factors lacking, but until they were obliged to alter their attitude, our textile manufacturers persistently gave preference to the products of English and German manufactories instead of to corresponding dyes of American manufacture.

The annual production of benzol in the United States amounted to about 3,000,000 gallons before the war; by the end of 1915, however, it had increased to about 15,000,000 gallons. A heavy production (25,000,000 gallons) of American benzol is now as-

²Jordan, *Journal of Industrial and Engineering Chemistry*, 8 (1916), 174.

³About 10,000 gal. of light oil are produced daily by the distillers of coal tar; the remainder of the production comes from the light oil plants listed in Table I.

sured,⁴ and, when the war ends, the output from our plants will be so abundant that it may become available as an automobile motor fuel.

The locations and capacities of the light oil plants in operation in the United States are given in Table I.

TABLE I.—LIGHT OIL (50-60 PER CENT BENZOL) PLANTS IN THE UNITED STATES.

Companies,	Location of Plants,	Capacity Gallons per day.
Allegheny Coke Co.	Glassport, Pa.	1,800
Briar Hill Steel Co.	Youngstown, Ohio (a) ..	4,500
Cambria Steel Co.	Johnstown, Pa.	6,000
Camden Coke Co.	Camden, N. J. (a) ..	12,500
Citizens' Gas Co.	Indianapolis, Ind.	3,000
Gulf State Steel Co.	Gadsden, Ala. (a) ..	2,200
Inland Steel Co.	Indiana Harbor, Ind.	4,800
Lackawanna Iron & Steel Co.	Buffalo, N. Y.	6,500
	Lebanon, Pa.	1,600
Laclede Coke & Gas Co.	St. Louis, Mo.	1,800
Lehigh Coke Co.	South Bethlehem, Pa.	6,000
Maryland Steel Co.	Sparrows Point, Md.	2,500
Milwaukee Coke & Gas Co.	Milwaukee, Wis.	2,000
New England Gas & Coke Co.	Boston, Mass.	5,000
Republic Iron & Steel Co.	Youngstown, Ohio	5,500
River Furnace Co.	Cleveland, Ohio (a) ..	9,500
Solvay Process Co.	Birmingham, Chicago, Cleveland, Detroit, Holt, Ala., Philadelphia, Leba- non, Pa., and Syra- cuse	(b) 40,000
Toledo Furnace Co.	Toledo, Ohio (a) ..	5,000
U. S. Steel Corporation.	Fairfield, Ala.	15,000
	Farrell, Pa.	6,000
	Gary, Ind., and Joliet, Ill. (a) ..	16,000
	Woodward, Ala.	2,000
Woolward Iron Co.	Youngstown, Ohio (a) ..	11,000
Zenith Furnace Co.	Duluth, Minn.	600

(a) Not yet in operation. (b) Approximate estimate.

Carbolic Acid.—The production of carbolic acid has recently increased largely, mainly owing to the demand for picric acid for war purposes. With the exception that the production of the works of Thomas A. Edison—about 12,000 pounds per day—is used in the manufacture of phonographic records, the large quantities of carbolic acid which have been produced have not therefore become generally available for domestic use. However, a number of American plants have lately begun production which can be used for other commercial purposes to the advantage of the nation, and still other sources of supply will soon be ready. An annual production of 10,000,000 lbs. is needed to supply the national demand.

Carbolic acid was not produced in this country in large quantity until after the outbreak of the war, but synthetic carbolic acid was manufactured by the Semet-Solvay Company from benzol at Syracuse, N. Y., in 1900 and the following years, in quantities up to 2,500 lbs. per day. This carbolic acid was synthesized into picric acid, which was purchased by the United States Government.

Naphthalene.—The production of naphthalene has increased to an unprecedented extent during the past year. Before the war, the production in the United States amounted to about 2,500,000 lbs., but it is now over 7,000,000 lbs. The normal American consumption is about 9,000,000 lbs.; but by the end of this year, the output of the American plants will undoubtedly be sufficient to insure an adequate supply for all

domestic needs, with the result that England and Germany shall thereafter be unable to export naphthalene to this country.

Aniline Products.—The five plants for the manufacture of aniline colors established in this country before the war, have, during the past fifteen months, extended their production to the utmost capacity in keeping with safety for the investments involved. Prior to the war these establishments produced a somewhat limited quantity of coal-tar colors, the annual output being about 3,300 short tons. For the purpose of their manufacture, intermediates were largely imported, principally from Germany. These were assembled into finished dyes by the aid of a few American chemicals and by the labor of about 400 workmen.

Before the war had continued a year, the output of American coal-tar colors had doubled, and at the present time it is, at least, three times the production before the war. This great increment involved an enormous increase in the production of coal-tar crudes, and it also induced the organization of companies for the manufacture of intermediates, especially of aniline.

The domestic supply of crudes has assumed quite large proportions. In December, 1915, the approximate monthly output, in short tons, was as follows: Benzol, 7,500; toluol, 1,870; xylol, 950; naphthalene, 12,500; and carbolic acid, 10,000 tons. The demand for benzol, toluol and carbolic acid to be used in the manufacture of explosives is at present so abnormally high that there has been considerable difficulty in obtaining sufficient supplies for the manufacture of coal-tar intermediates. Nevertheless, the manufacture of these latter, especially of aniline, has suddenly grown to considerable proportions and it is constantly increasing. There are at least twenty concerns engaged in this branch of manufacture and one is constantly learning of others which are contemplating entrance into the field. Approximately an equal number of firms is now engaged in making finished coal-tar dye-stuffs. Synthetic indigo is being manufactured at Midland, Mich.

Potash.—During 1915, steps were finally taken to produce salts of potassium from mineral sources on a commercial scale in the United States. It is probable that Searles Lake in San Bernardino County, California, will be the most important American source of potash, but the war condition enabled other sources to be hastily developed. The alunite deposits near Marysvale, Utah, thus became the first important producers of potash in this country. The production of potassium sulphate on a commercial basis was begun at Marysvale in October, 1915, by the Mineral Products Corporation, and this concern is contemplating doubling its present capacity.

The Searles Lake potassium-bearing brine will, in the near future, be treated for the commercial production of potassium salts and borax. Work has also

been begun which will probably eventuate in the commercial recovery of potassium salts from the brine of the Great Salt Lake in Utah. In their present development, practically all of the producers of potassium salts are employing war-time processes which could not compete with the German producers on a pre-war basis. However, it is possible that potash will never be so cheap as it was before the war, for it is one of those commodities on which it will be most easy for Germany to levy and collect taxes in the future.

The scarcity of potash has caused a renewal of interest in the growths of kelp on the Pacific coast, regarding which much has appeared in the technical and popular press. Before this year most of the companies attempting to develop the kelp industry have been of limited capital. Recently, however, several concerns with, it is reported, adequate capital to carry their developments through to a successful issue, have engaged in this industry, so that at the present time a limited amount of dried kelp is being produced and a considerable increase in this production is shortly expected. One of the prominent packing companies of Chicago has a kelp potash plant in operation at San Diego, Cal.

With the present high price of potash, it is said that the drying of kelp is a profitable business. It is predicted that such conditions will enable the industry to get a start and to work out its numerous problems. With normal prices of potash, kelp must be worked in plants of large capacity, well designed, with a minimum of labor, and every possible economy effected. All of the profitable by-products (iodine, algin, etc.) must be saved. Laucks⁵ is of the opinion that if, even after the war, the price remains above \$35 per ton for 80 percent muriate of potash, kelp can be worked at a profit in a properly designed plant.

Potash is now being recovered in the cement industry, and the manufacture of potassium salts from the refuse of molasses is to be begun in Colorado.

Barium Products.—Before the war about 40,000 tons of barite were annually shipped to the United States from Germany, and practically all of this considerable importation was used in the manufacture of lithopone, which was the only barium product made on a large scale in this country up to the time of the European conflict. It is said that there are now six manufacturers⁶ engaged in the production of large quantities of lithopone from barite supplied from deposits in the State of Tennessee, Kentucky, Virginia and Missouri. Five American companies are also manufacturing barium compounds (chloride, carbonate, hydroxide, nitrate, and dioxide of barium⁷), thus giving still further production to American mines—possible double the quantity of barite formerly im-

ported. Stone⁸ has stated that with the manufacture of barium salts we have a practically new industry which will make us independent of Europe in the future.

The war has had a salubrious effect on many of our well-established industries. It has, in fact, given rise to a general prosperity in certain lines which is most agreeable to those who live secure from the immediate calamities of it.

In particular, our munition plants have been hyperactive. It may be noted here, however, that four of the largest establishments are now turning out considerable orders for the United States, in spite of the enormous foreign orders which were reported to make work for our own Government entirely out of the question.

Mineral Acids.—There has never been any foreign competition on sulphuric, nitric and hydrochloric acids, mainly because of the heavy transportation charges, American manufacturers being able to make these acids at prices which render their importation unprofitable. Until about the middle of 1915, American manufacturers were entirely able to supply the needs of the country as usual; but as the war continued and the demand for munition purposes gradually increased, the requirement for acids became so urgent that the manufacturers thereof have found great difficulty in supplying them. As a consequence, many American consumers are unable to secure enough supplies to conduct their technological operations; or when they do get sufficient for their present business, they are unable to obtain any additional quantity for an increased business, so that the acid situation has been and is a very serious one indeed.

A prominent manufacturer of barium products stated several months ago that he has been unable to take contracts on barium chloride, nitrate of sulphate because it is absolutely out of the question to obtain the necessary acids. "The people with whom we have dealt for our acids for years are simply either refusing to give us any material or are supplying us with ridiculously small lots at enormous prices, for there are other channels which buy larger quantities and pay more than the peaceful manufacturer can afford."

War demands for sulphuric acid have stimulated the production of the great Tennessee acid plants to a maximum, copper being in reality only a by-product now. A number of important additions have been made to these and to numerous other sulphuric acid plants. The advance in both sulphuric acid and potash has put up the price of complete fertilizer and bulk acid phosphates, so that Tennessee phosphate properties have been stimulated both as to production and as to efforts to decrease metallurgical losses. Since the price of sulphuric acid began to advance, a number of the manufacturers of fertilizers have in-

⁵Met. Chem. Eng., 14 (1916), 308.

⁶Two of these are located in Tennessee: the Durex Chemical Works at Sweetwater and the Clinchfield Products Association at Johnson City.

⁷The consumption of "barium dioxide" is large, for the value of the hydrogen dioxide used annually in the United States amounts to \$8,000,000. Before the war, England supplied much of the barium dioxide used by the manufacturers of hydrogen dioxide.

⁸Journal of Industrial and Engineering Chemistry, 7 (1915), 992; see also Toch, *Ibid.*, 993.

stalled acid plants at their works, which indicates that the ruling quotations on sulphuric acid are more or less above the figure at which they think they themselves can produce it. For instance, one company producing superphosphate in Baltimore now has an output of 300,000 tons of acid per year.

Because of the large markets for sulphuric acid, its production from waste gases is now carried out at copper smelters in Arizona and California, as well as in Tennessee; and by-product acid from the sulphurous fumes of zinc smelters is being made at ten places in Colorado, Illinois, Indiana, Kansas, Ohio, and Pennsylvania. Liquefied sulphur dioxide is now being produced by the Virginia Smelting Company, of West Norfolk, Va., and the demands of the sulphate pulp industry may give rise to the recovery of sulphur dioxide at other metallurgical plants.

As indicated above, to insure the presence of our chemical self-containedness, it will be necessary to manufacture nitric acid from the air on a suitably large scale, and magnificent water power is available at a number of accessible points for the establishment of this industry. It was in the founding of electrochemical industries upon a grand scale at Niagara Falls that the United States first disclosed her latent power as a factor in the field of chemical industry; but we may derive much profit by careful study of the systematic and exhaustive manner in which the water power of Norway has been regulated, stored up, and pressed into the service of applied electrochemistry. Let us hope that industrialists will avail themselves of this opportunity and will enlist the services of our best technical talent. The Pauling process is in operation on a small scale (4 tons per day) at Great Falls, N. C., by the Southern Electrochemical Company, and the field invites the invasion by modern industrialism.

Ammonium Sulphate.—The production of ammonia, calculated as ammonium sulphate, in the United States during 1915 is estimated to have been 212,000 tons, an increase of 17,000 tons upon the actual output in 1914. It is further estimated that approximately 80 percent of the 1915 output was from by-product coke plants, and in view of the demand for coke and coal products chemicals it seems certain that a further substantial increase in output of ammonium sulphate in the United States must be counted on in 1916.

It is predicted that the question of sulphuric acid supplies will become more acute as the demand for ammonia for munition purposes increases, and there must therefore be some shrinkage in the production of ammonium sulphate; but munition manufacturers are able to use concentrated ammonia liquor instead of ammonium sulphate, so that no handicap will result.

Sodium Compounds.—About 1,500,000 tons of caustic soda, soda ash, and bleaching powder are now being manufactured in the United States. For a short period after the war, American manufacturers were

able to continue their supply of these products in the ordinary way; but the cessation of shipments of sodium compounds from European countries to other countries by reason of the war, eventuated in a demand for American products to supply this shortage. A large export business has thus been established by the American manufacturers and great prosperity has resulted.

In March, 1915, the stocks of soda ash in this country had accumulated to such an extent as to create a depressing sentiment among producers and to urge the most heroic measures of relief. Plans had been formulated to undertake the development of increased outlets in South America; but before the foreign trade campaign could be initiated, the market underwent a complete change. The importance of soda ash as a war munition factor was the turning development, and with England, normally the mainstay of foreign consumption, conserving home supplies for its own exigent needs, the export demand for the American product and the stimulus to the domestic manufacture of explosives soon made heavy inroads upon the holdings in this country. The effect of these factors has been emphasized during the last few months by the increased requirements in the fields of regular consumption, namely, the soap, paper, glass, textile and petroleum industries. Confidence has been expressed that a good share of the business in soda ash, directly or incidentally due to the war, will be retained upon the restoration of peace; but there are not known to have been undertaken any definite plans for additional equipment on the strength of enduring trade in the product on anything like the present volume. In March, 1915, soda ash was procurable at 57½ cents per 100 lbs., on the basis of 48 per cent; by the close of 1915, \$1.85 was in effect. The developments since the first of the year have resulted in a more stirring range of prices, principally through the control of the open market by second hands, who now maintain 4 to 8 cents per pound flat, for a 58 per cent test.

Caustic soda has attracted much interest because of the part which it plays in the manufacture of picric acid; in fact, it is principally through this medium that the reformation of soda ash has been accomplished. At the present time, supplies of caustic soda are reported to be slightly freer than those of soda ash, but they are well controlled, with second hands dominating the market for prompt delivery. The question of increasing the production of caustic soda is involved in the difficulty and uncertainty of soda ash supplies. The premium on bleaching powder would prove an incentive to the production of caustic soda by the electrolytic process; but those manufacturers who employ the old method yielding straight caustic soda, are said to have the advantage of large supplies of soda ash.

Other products now manufactured in this country are ferro-cyanides of sodium and potassium, sodium

and potassium chlorates, and sodium and potassium dichromates; and the manufacturers of these salts hold the whole American trade, for there are practically no importations from abroad. The manufacture of potassium ferrocyanide has been limited, owing to the inability of American manufacturers to secure potassium salts from Germany; consequently, most of them are said to be working almost exclusively on soda, and the paint manufacturers, who are large users, have attempted to produce their Prussian blue from the sodium salt instead of that of potassium. At the present time the domestic output of sodium ferrocyanide is fully engaged without beginning to satisfy requirements; but relief to the prevailing stringency is expected upon the arrival of imports.

The manufacture of sodium chlorate and dichromate has continued* in increasing quantity during the past year, but the production of potassium chlorate and dichromate has been limited, owing to the inability of the manufacturers thereof to secure proper quantities of potassium chloride from Germany. The sodium salts have been substituted wherever possible. Contracts for sodium dichromate are now being made on a basis of 20 to 22 cents, as against $4\frac{1}{2}$ to $4\frac{3}{4}$ cents for 1915, and the producers have withdrawn all offers for forwarding delivery. The heavy export trade has been the principal factor for the unusual position of the market, supplemented by the influence of chrome ore.

Glass.—A wonderful prosperity obtains in the American glass industry. This is mainly attributable to the war, which shut off importations from Belgium, France and Germany, and thus permitted American manufacturers to build up an export trade with neutral countries formerly supplied by the belligerents; but the domestic demand for glass products has also greatly increased—to such an extent, in fact, that selling agencies have withdrawn prices and the “hand” window glass plants may be operated during the coming summer months.

The Tables II and III of imports and exports are clearly indicative of the effect of the war on this industry.

TABLE II.—THE VALUE OF U. S. GLASS AND GLASSWARE TRADE DURING THE SEVEN MONTHS ENDING WITH JANUARY, 1916, COMPARED WITH THE PREVIOUS YEAR.

Article.	Imports.		Exports.	
	1915.	1916.	1915.	1916.
Bottles, plain	\$ 529,779	\$ 379,095	\$ 375,275	\$ 1,036,109
Bottles, ornamented	366,305	157,771		
Window glass	583,880	121,157	393,980	1,342,870
Plate glass	93,384	394	242,292	897,793
Optical, dutiable	233,585	90,546		
Optical, free	301,130	146,045		
All other	1,108,276	353,858	1,291,984	3,031,208
Total	\$3,216,339	\$1,239,866	\$2,243,531	\$6,307,980

TABLE III.—THE VALUE OF GLASS EXPORTS DURING JANUARY, 1916, COMPARED WITH JANUARY, 1915.

Article.	1915.	1916.
Bottles	\$ 47,083	\$178,884
Window glass	140,571	229,797
Plate glass	70,275	56,776
All other	156,761	505,668
Total	\$414,690	\$971,125

Chlorides of Carbon.—The manufacture of carbon tetrachloride has greatly increased in this country since the war. At the inception of hostilities the American manufacturers were probably producing one-half of the national consumption. Since the war they have greatly enlarged their plants, so that they are said to be now supplying all of the American trade; the consumption of carbon tetrachloride is continually increasing, but those in touch with its manufacture state that even after the close of the war the whole consumption of the United States will be manufactured here.

At the present time the production of the chlorides of carbon is mainly dependent upon the availability of supplies of carbon disulphide. Just as soon as an economic process for chlorinating natural gas rich in methane is available, the latter will probably supplant carbon disulphide.

Oxalic Acid.—The manufacture of oxalic has been much developed in this country during the past two years. A plant was established a number of years ago at Bradford, Pa., but up to the time of the war it constantly experienced trouble in competing with the European product because of the reduction of duty in the last tariff. However, since the war practically stopped the importation of foreign acid, the whole American consumption is now reported to be taken care of. At the present time there is a considerable shortage in supply of oxalic acid and the price is therefore high; but eventually this product will be manufactured to the full extent of the American consumption and the business will be held here.⁹

Steel Industry.—The steel mills are being operated on an unprecedented scale, and the great demand for ferrous products has been aptly compared to the days of activity in Pittsburgh in Civil War times, when, however, the mills were fewer in number than they are at present and there was no Gary or Birmingham to increase the nation's output of steel products. During the past year numerous lines of steel have more than doubled in value, but nation-wide buying still goes on apace.

The annual report of the Bethlehem Steel Corporation for 1915—the first full year of the war—illustrates the turgid prosperity obtaining in the field of ferrous metallurgy. The net income of the year amounted to \$17,762,812.61, as compared with \$5,590,020.18 for 1914. The orders on hand on December 31, 1915, amounted to \$175,432,895.19 against \$46,513,180.95 on the corresponding date in 1914. The average number of employes in the United States in 1915 was 22,064 against 15,586 in 1914.

During March, 1916, the Carnegie Steel Company, with its equipment of 59 blast furnaces, was operating all but four of them. These four were being repaired, but the company, in operating 93.38 per cent of its total furnaces, surpassed all former records. It may be mentioned here that all of the active stacks

⁹Stone, loc. cit.

of the Carnegie Steel Company have been modernized and are now producing more than 120 per cent of their original capacity as a whole.

The total number of American furnaces in blast at the close of 1915 was 310, against 236 reported at the end of the first half-year. The production of pig-iron in 1915 (29,916,213 gross tons) was the largest ever reported in the United States, with the one exception of 1913; it amounted to nearly twice that of fifteen years ago. Increasing numbers of inquiries are constantly coming in from foreign buyers, mainly in Italy, for large lots of Bessemer pig-iron.

At the present time a famine exists in the ferro-alloy market, owing to the fact that the war has excluded much manganese from English sources and all the German supplies. Ferro-manganese, which sold at \$38 a ton when the war broke out, is now being sold at steel centers for spot shipment at \$350 a ton and on contract sale covering a certain period of delivery at \$175 a ton; but willing buyers are unable to purchase much even at these fabulous figures. Next to carbon, manganese is the most important ingredient of steel; hence, with its price increased from 1.9 cents a pound to 8.75 cents a pound, its influence on the rising cost of steel is clearly apparent. War-time conditions have made the demand in this country for manganese ore the greatest in history, causing the searching out and the development of the limited domestic deposits as never before in the economic history of the nation.

Tungsten has also advanced to high levels, and consequently its ores are in very strong demand. As high as \$90 per unit has been paid for prompt delivery of ore carrying 60 per cent of WO_3 , and \$110 per unit has been offered for 65 per cent concentrates, but even such high prices have apparently failed to bring out new supplies. Of interest is the advertisement of the largest producer as well as consumer of tungsten ores in this country, that the highest prices will be offered for all kinds of tungsteniferous minerals. Perhaps tungsten ore from South American sources may solve the problem of increasing the supply.

The tremendous activity which obtains in the ship-building of the United States has advanced steel plate prices up 147 per cent since the war began. Then, too, car builders are operating their plants to capacity whenever it is possible to obtain steel. In one case, a prominent car construction company was obliged to withdraw its bid on 4,000 steel freight cars because it was totally unable to obtain steel for them under the contract time of delivery. The war devastating Europe has also been responsible for considerable of the activity enjoyed by the manufacturers of wire products.

California magnesite is being calcined for use in open-hearth steel furnaces; but at the close of the war this will probably be discontinued and the Austrian supply will be resumed.

Zinc.—Perhaps the most important commercial fea-

ture in connection with zinc smelting since the commencement of the war, was the expansion of the United States Steel Corporation, through its subsidiary, the Edgar Zinc Company, into the zinc-producing field. The new Donora, Pa., plant of this corporation has a smelting capacity of 100,000 tons of zinc ore annually and a productive capacity of about 40,000 tons of spelter.

The total production of spelter by ore smelters in 1915 was 507,142 tons, against 370,312 tons in 1914. The production by quarters showed a steady increase, especially in the second quarter, when the important new plants of 1914—Rose Lake and Langeloth—began to strike their gait, when several of the older smelters began to start new furnaces and when the resumption of work in several previously idle plants—particularly Caney, Dearing, and Altoona—began to count largely in the production. In the third quarter several of the small coal smelteries of earlier times, one or two new ones, and some of the older natural gas plants began operation.

TABLE IV.—THE PAST AND PRESENT MARKET VALUES OF VARIOUS STOCKS (a).

Prices of Common Stock.			
"Ordinance Stocks."	July 30, 1914.	June 4, 1915.	April 10, 1916.
Bethlehem Steel	30	149	465
Bliss (E. W.)	85	340	420
Canadian Explosives ..	88	330	350
Colts Patent Fire Arms.	165	360	825
Du Pont (E. I.) Powder	120	410	252
Electric Boat	15	80	370
Hercules Powder	120	231	390
Savage Arms	120	172	...
Winchester Arms	1,190	1,570	2,000
Other "War Stocks."	July 30, 1914.	June 4, 1915.	April 12, 1916.
Allis Chalmers	6	17	28½
American Car & F'dry.	44¾	55	67¾
American Can	19¾	43	60¾
American Locomotive ..	20¾	50	76¾
Baldwin Locomotive ..	41	52	104½
Crucible Steel	14½	32	92
New York Air Brake ..	60	88	141
Pressed Steel Car	34	49	51
Westinghouse Air Brake	120	129	137

(a) It is impossible to furnish a complete list of the quotations on "chemical stocks" prior to the war, for many of these issues were traded in only through the secretaries or directors of the companies between stockholders and no official records are available. However, the following information was supplied by Messrs. Gilbert Elliott & Co., of New York, on March 20, 1916:

"The tremendous rise in 'powder stocks' since the war commenced has been closely paralleled by the advance in 'chemical stocks.'

"General Chemical, for instance, has advanced from a low of 163 last year to 310 at present. On Feb. 1 the Company paid extra dividends of 15 per cent on the common stock. Semet-Solvay, which was selling around 90 early in 1915, is now selling at 325-350, after having increased its capitalization by a stock dividend of 100 per cent. This is equivalent to 650-700, or a sixfold increase. Dow Chemical sold around 135-140 a year ago, and recently reached \$500 per share. The Company declared a dividend a few days ago of 60 per cent on the common stock, payable two-thirds in preferred stock and one-third in cash. Grasselli Chemical sold at about 120 in 1913, compared with a present price of nearly \$300. Last year the company paid a 10 per cent stock dividend. Many of the chemical stocks reaping the benefit from war prices for chemicals, which in some cases represent a 1,000 per cent increase over normal, have hitherto been so closely held that a comparison of prices is impracticable. However, it is interesting to note the high prices which are at present bid for representative stocks of this character, viz.: Union Sulphur, 4,400; National Aniline & Chemical, 490; Dow Chemical, common, 465; Freeport Texas Sulphur, 400; Solvay Process, 300; and Smith Chemical, 225."

Tin Smelting in the United States.—The United States imports normally about 45,000 tons of tin annually, and of this quantity about 90 per cent is Straits tin, which is largely consumed in the manufacture of tin plate. The Straits Settlements impose a protective export duty on tin ores, thus compelling the reduction to metal in the country in which it is produced. Several years ago a tin smeltery was built at Bayonne, New Jersey, but about the time it was completed this duty was imposed, so the works never operated.

Apart from the Straits Settlements, Bolivia is the largest producer of tin ore, but Bolivian ore contains impurities which, with the established method of smelting, do not permit the production of a tin suitable for tin plate. During 1915, however, the American Smelting and Refining Company began the erection of a plant at Perth Amboy, New Jersey, which is not only to smelt the impure ores from Bolivia and elsewhere, but is also to refine the product by an electrolytic process.

The tin plate capacity of certain of the companies in the Pittsburgh district was increased during 1915 and the early part of 1916. The Standard Tin Plate Company, of Canonsburg, Pa., completed 10 new mills; the McKeesport Tin Plate Company, of McKeesport, Pa., built 20 new mills; and the Phillips Sheet and Tin Plate Company, of Weirton, W. Va., the Wheeling Steel and Iron Company, of Yorkville, Ohio, and several other companies added mills to their plants. While the price of all commodities entering into the manufacture of tin plate, including steel, pig tin, palm oil and sulphuric acid, advanced considerably during the past year, and certain of the companies have at times experienced difficulty in securing supplies of these materials, the market is strong and the outlook is generally regarded as satisfactory.

Aluminum.—The Aluminum Company of America has enjoyed much prosperity during the past two years, and it has in consequence greatly increased its capacity. A big water power, estimated at 800,000 h. p., is being developed on the St. Lawrence River, and the plant of the Southern Aluminum Company at Whitney, North Carolina, which was taken over during the past year, is being completed. The Aluminum Company of America is said to be bending every energy to increase its output, and it is thought that when its new works are finished whatever pressure now exists for an additional supply of aluminum will be relieved. This company is proceeding on other substantial enlargements for 1917 and the following years. While it is said that it has not sold any aluminum for munition or for war purposes, nevertheless considerable resold aluminum has gone out of the United States for this purpose, being derived partly from aluminum transmission wires which have been replaced by those of copper.

The extreme demand for aluminum from Europe arose partly from the increase in the use of am-

monal, a mixture of ammonium nitrate and powdered aluminum, which is used in large quantities as an explosive by the European belligerents.

Antimony.—For a number of years the consumers of this country have been accustomed to buying Cookson's and Hallett's antimony to the exclusion of nearly every other brand. With the outbreak of the war, however, Great Britain required all the antimony its smelters could produce; and although shipments have been reaching this country from England, they are made under special permit, difficult to obtain. During 1915, Chinese antimony was introduced to the American market, and next to China, Japan now sends the largest quantities of antimony here.

The high prices for antimony in 1915 induced several American concerns to engage in the smelting of its ores. Among the most important of these are the Western Metals Company, of Los Angeles, Cal., which is managed by persons who were previously connected with Cookson & Company, Newcastle-on-Tyne, England; and the Merchants Finance Company, of Harbor Industrial City, Cal. Antimony smelting has also been started on the Atlantic coast, the Magnolia Metal Company having inaugurated smelting in Brooklyn during 1915. Great difficulty has been experienced in securing suitable ores. China no longer ships antimony ore, Australia has put an embargo upon its shipment, and competition for the South American ore has been very acute. Transportation difficulties in Alaska are the main obstacles to obtaining the supplies of antimony ore from there, although the Alaskan ore is of exceedingly good quality. During 1915, antimony mines in all parts of the United States were therefore rejuvenated and several small furnaces were built. Stibnite deposits are being worked north of Neuralia, in Kern County, California, and also at Wild Rose Spring, northeast of Trona, California. While several smelteries operated in Mexico during the past year, no attempt has been made to exploit the great deposit of jamesonite which exists there; however, this deposit will undoubtedly be drawn upon in the future.

It is said that approximately 12½ per cent of the present production of antimony is used in the manufacture of war supplies.

Mercury.—The production of mercury in the United States in 1915 amounted to 20,681 flasks, compared with 16,548 flasks in 1914. This production was chiefly derived from California.

The mining of quicksilver was at one time an important industry in California and may become so again if the investor is given reasonable assurance of a tariff which will permit him to operate in fair competition with European producers after the embargo is lifted and conditions again become normal. It is said that a reasonable import duty to compensate for the different labor conditions would probably double the California production within a period of two years. This production may not be of great importance outside of California, provided the United States

can always be certain of obtaining adequate supplies for Government uses in times of emergency. However, for the time being we are cut off from foreign supplies, and the state of the market indicates that it might be a difficult matter for even the Government to accumulate any considerable reserve stock for the manufacture of fulminates and antiseptics. The production, not only of California, but of all North America, is now far short of the ordinary requirements of the United States in times of peace. These requirements are in the neighborhood of 25,000 flasks per year and seem to be increasing.

During 1915 the output of California amounted to 13,916 flasks. The remainder of the small American production came from Nevada and Texas; but with the active prospecting and development which have continued in these states since the beginning of 1915, it is probable that their total outputs will constantly increase. Then, too, the California State Mining Bureau has under investigation the concentration of and the application of flotation to cinnabar, and the results of this inquiry may serve to encourage additional development.

A prevailing illusion, especially among people living outside the "big prison," as the economist Naumann refers to the "self-contained commercial state," is that, when the military resources of the European contestants are exhausted, and peace is established owing to the depletion of their martial energies, war is to cease. It is conceded that as a military enterprise it will be concluded when one or the other side perceives that it is hopeless to gain anything further, and will, in consequence of this forced attitude, be desirous of making concessions for the sake of peace; but it is certain that the great economic contest, waged with such vigor for several decades, will be resumed with renewed intensity. This world battle will be fought by trained men in laboratories, mills and commerce, just as the present war has been fought by trained men who have behind them superior capacity in shop and office.

Germany, the "big prison," is arming for this new war, which will be not merely a struggle for the existence of her economic power, but rather a fight for the full development for the future of her inheritance of science, technical ability and organizing capacity. In her efforts for industrial and commercial recuperation, Germany will therefore be strenuous to find markets for her enormous capacity of chemical production. Great Britain and Russia, former great customers, will be lost to her, and other belligerent countries may close their ports to her. The inquiry therefore arises, where is Germany to market her surplus manufactures?

In the past Germany has demonstrated not only a marvelous industrial efficiency but a remarkable capacity for intimate and effective commercial partnership between private initiative and government support. In 1870, her export trade amounted to only \$350,000,000 per year. At the outbreak of the pres-

ent war she was the possessor of a world trade of \$2,500,000,000 per year. At the present time her industrial structure is intact and she has acquired possession of land of great natural wealth. She has already lost custom, and it seems probably that for some time the bitterness engendered by the present conflict will not make "made in Germany" a recommendation among the allied powers and their colonial possessions. To what market will Germany therefore turn under the stimulus of her necessity? One can only conclude that she will endeavor to establish herself in South America and in our own alluring domestic market.

This is not, however, the entire problem. The present antagonists of Germany will, in their battle for rehabilitation, have heavy debts to pay. In consequence whereof, they will be in every market her active rivals, and will enter into this competition not only with new and greatly intensified motives, but with increased efficiency. To quote an English statesman, "We have introduced scores of millions worth of automatic machinery which will have an enormous effect upon our industries when the war is over." It follows, therefore, that the United States shall have much to face, and this realization brings us to the consideration of our industrial defenses.

Economists urge that we do not base our expectations upon the present commercial tumidity, which is essentially abnormal. Moreover, every month of the continuance of the war must enormously inflate present prices and consequently increase the risks of the inevitable reaction. It is true that in the amount of our exports we are at present leading the world, and it is agreed on all hands that for some time after the war a great demand must continue for certain of our products, as, for example, structural materials; but there are obvious reasons. If it were not for the alimental influences of the war, we should be today as we were at the beginning of 1915, limiting our enterprises and endeavoring to provide for idle workmen.

It is clear from the conditions obtaining in Europe that when the present belligerents once enter upon the struggle for industrial and commercial recuperation, they will lower their prices to a point which will enable them to procure ready markets. Their governments will urge upon the people, as an obligation of patriotism, the extension of the laboring day, the acceptance of lower wages, and the reduction of the profits of business for the purpose of securing markets for their products. We must therefore actively prepare for this coming commercial war. At this time, when expert knowledge and trained skill constitute the chief buttress of national defense, it is our industrialists who must lead in the great work of preparation. Provided they are extended reasonable guarantee for the future and are permitted to solve in their own way the great problem of world competition on the basis of a secure home market, American manufacturers shall be able to get our industrial defense in readiness; but prompt action is required if we are to avoid the dire consequences of the coming contest.

COST OF MAKING GASOLINE BY THE RITTMAN PROCESS.

The U. S. Bureau of Mines has recently given out the following estimate on the cost of making gasoline by the Rittman process. They are based on a 5-tube plant and are the result of a 5-day run with a recovery of gasoline of 17 per cent and with varying prices of fuel oil.*

The capacity of a single tube was 1.55 bbls. per hour or 37.2 bbls. for 24 hours. With loss, 10 per cent, would yield 17 per cent gasoline, the balance being fuel oil, as valuable as original fuel oil.

The estimated cost of a five tube plant.....\$15,000.00
Estimated cost of building to house plant..... 5,000.00

Total\$20,000.00

Monthly capacity 5,580 bbls. Deducting about 10 per cent for "shut downs" leaves net capacity 5,000 bbls. Yield of gasoline 17 per cent, 850 bbls., or 35,700 gals. Loss, 10 per cent, equals 500 bbls. Residuum, 73 per cent, equals 3,650 bbls.

COST OF FUEL OIL \$0.50 PER BARREL.

Expense—

5,000 bbls. fuel oil at \$0.50 per bbl.....\$2,500.00
Labor for one month 500.00
Fuel (1,050 M ft. at 15c) 160.00
Electricity 100.00
Repairs 100.00
Interest and depreciation, 6 per cent each..... 200.00
Refining cost 20c per bbl..... 1,000.00

\$4,620.00

Credit—

3,650 bbls. residuum at 50c (fuel oil)..... 1,825.00

Net cost—

Net cost of 850 bbls. (35,700 gals.) gasoline.....\$2,795.00
Cost of gasoline per gal., 7.8c.

COST OF FUEL OIL \$1.00 PER BARREL.

Expense—

5,000 bbls. oil at \$1.00.....\$5,000.00
Labor 500.00
Fuel 160.00
Electricity 100.00
Repairs 100.00
Interest and depreciation, 6 per cent each..... 200.00
Refining cost 1,000.00

Total cost\$7,120.00

Credit—

3,650 bbls. residuum at \$1.00 (fuel oil)..... 3,650.00

Net cost—

Net cost of 850 bbls. (35,700 gal.) gasoline.....\$3,470.00
Cost of gasoline per gal., 9.74c.

COST OF FUEL OIL \$1.47 PER BARREL.

Expense—

5,000 bbls. oil at \$1.47.....\$7,350.00
Labor 500.00
Fuel 160.00
Electricity 100.00
Repairs 100.00
Interest and depreciation, 6 per cent each..... 200.00
Refining cost 1,000.00

Total cost\$9,470.00

Credit—

3,650 bbls. residuum at \$1.47 (fuel oil)..... 5,365.00

Net cost—

Net cost of 850 bbls. (35,700 gal.) gasoline.....\$4,105.00
Cost of gasoline per gal., 11.5c.

*Fuel oil is oil from which gasoline has already been extracted by ordinary process of refining.

COST OF FUEL OIL \$2.10 PER BARREL.

Expense—

5,000 bbls. oil at \$2.10\$10,500.00
Labor 500.00
Fuel 160.00
Electricity 100.00
Repairs 100.00
Interest and depreciation, 6 per cent each..... 200.00
Refining cost 1,000.00

Total cost\$12,620.00

Credit—

3,650 bbls. residuum at \$2.10 (fuel oil)..... 7,665.00

Net cost—

Net cost of 850 bbls. (35,700 gal.) gasoline\$4,955.00
Cost of gasoline per gal., 13.9 cts.

HYDROGENATED OILS IN THE SOAP INDUSTRY.*

By CARLETON ELLIS.

The developments in oil hydrogenation have brought to the soap industry an innovation of fundamental importance in the domain of raw materials. The soap manufacturer, no longer well able to purchase the best grade of fats in face of the high prices paid by the margarine and other fat edible industries, has now at his disposal the means for utilizing lower grade materials in substitution for more costly stock.

By hydrogenation, oils which formerly made soaps only of soft consistency, now yield the more valuable hard soaps. This has led to a very rapid development of the art with respect to the production of soap making fats. In particular, fish and whale oils have been made use of, because these oils may be completely deodorized by the addition of hydrogen.

According to a Japanese chemist, Tsujimoto, the odor of fish oil is due almost entirely to a fatty constituent and not to so-called impurities. This fatty constituent is clupanodonic acid having the formula $C_{18}H_{28}O_2$, which, therefore, by the addition of 8 hydrogen atoms, becomes stearic acid. When hydrogenated down to an iodine number of about 50, fish oil has the consistency of hard tallow and the odor of fish oil is wholly absent. Even the fishy taste is scarcely in evidence.

For soap making, this product is satisfactory, as it complies with the test for a deodorized fish oil suitable for soap making in that the odor of the original oil is not apparent when ironing laundered goods on which such soaps are used. If, however, at least with the poorer grades of oil, the hydrogenation is not carried on to a point where the iodine number is approximately 50 or less, there is some danger that the fishy odor will become apparent during the ironing operation.

It appears not improbable that unstable odor-forming nitrogenous impurities in fish oil add hydrogen during the hardening process and are transformed into bodies of a stable character.

A German-Norwegian company, capitalized at about

*From The American Perfumer.

\$833,500 organized to work a new German method for hydrogenating whale oil has commenced operations at Fredrikstad, Norway. The Hafslund Falls are being utilized to generate the electric power required by the work and also to manufacture by electrolysis the hydrogen required for the hardening process to which the purified whale oil is submitted and converted into a solid neutral fat. The daily consumption of oil is about 300 barrels.¹ (Jour. Ind. and Eng. Chem., 1913, 608.)

Samples of Norwegian hydrogenated whale oil which have come to the writer's attention are of exceptionally high quality.

Whale oil of the grades known as 0 and 1 hydrogenate readily with nickel as a catalyzer. No. 2 is somewhat more difficult, and No. 3 is decidedly troublesome of treatment without special refining.

Auerbach (Chem. Ztg. 37, 297) considers the hydrogenation process responsible for an advance in the price of fish oils so that they will be of doubtful benefit to the soap industry. Also he states that the so-called burned odor which was noticeable in soap made from hardened fats is said to have been overcome. Besides fish and whale oils, he notes that castor oil is used for insulation purposes in the electrical field.

The commercial side of fat hardening is discussed to some extent by Schicht (Seifen Ztg. 1913, 287) and the value of fish and whale oils in this field is considered.

As Dr. Holde states (Seifen. Ztg. 1912, 918), oleic acid, the most important constituent of all semi-drying liquid oils, requires only 2 parts of hydrogen to 282 parts of oil in order to get stearic acid, while linoleic and linolenic acid require 4 and 6 parts, respectively, to 280 and 278 parts. Ricinolic acid, which contains one atom of oxygen more than oleic acid, forms an oxystearic acid which has a very high melting point, but which also only contains 2 atoms more of hydrogen than the original acid. The glycerides of stearic or palmitic acid naturally remain unchanged throughout the operation.

In this country very little has as yet appeared in the literature regarding the application of hydrogenated oils in soap making, but in Germany considerable space has been given by the trade journals to discussions of the subject. Some of the statements are of a very contradictory character, as is, of course, to be expected in the early stages of development of this important subject, especially in view of the very considerable degree of empiricism which prevails in some branches of the soap making industry.²

¹The Knowles Oxygen Company, of Wolverhampton, England, has contracted with the Sunlight Soap Factory, in Port Arthur, to erect an annex to the plant for the production of the hydrogen necessary for hardening palm oil; the oxygen is to be collected and sold.

²In England one large concern is offering several grades of hardened fat ranging as follows:

	Iodine.	M. P.	Titer.
A1	50	40-42	36
A2	55	23-30	32
C1	60	44-46	45
C2	75	35-37	36

It is to be regretted that so much of the published matter relates to the products of one concern, the Talgol, Candelite and similar hydrogenated fish and whale oils, etc., of the Germania Oelwerke at Emmerich, but while soap making as practiced in Germany differs considerably from the practice in this country, it is believed the work abroad will prove at least suggestive if not instructive.

In the following an attempt has been made to briefly review the more important contributions in this connection.

Garth (Seifen, Ztg. 1912, 1278) states that fish and whale oils are the raw materials for a considerable proportion of the hydrogenated products which up to the present time have found application in soap making. Being relatively low priced raw material many attempts have been made to make cheap soaps from fish oil. These attempts in the past have been unproductive because the objectionable odor reappears after goods are laundered. Hence there are many proposals directed toward the production of doorless fish oil. As is known, fish oil contains nitrogenous compounds and certain of the lower fatty acids arising from decomposition of the fish before the oils are expressed. Most of the proposals are based upon the assumption that these sources of the evil odor can be removed by the action of energetically reacting bodies, such as sulphuric acid and the like. However, neither treatment with strong acids nor distillation with superheated steam produce unobjectionable products. By hydrogenation the disagreeable odor disappears; nevertheless, there always remains an odor similar to that of distilled olein which, however, is completely concealed if the product is worked up with a goodly proportion of other fats.

Garth (Seifen, Ztg. 1912, 1279) observes that the hydrogenated fats which have been used in the soap manufacture appear in the trade as Talgol, Talgol extra, Candelite, Candelite extra, Crotolein Talgin, etc. Talgol has a melting point of 35-37° C. and an iodine number of 65-70. Talgol extra melts at 42-44° C., and the iodine number is 45-55. The Candelite products are harder, Candelite melting at 48-50° C. and having an iodine number of 15-20, while Candelite extra melts at 50-52° C., and exhibits an iodine number of 5-10.

Heller (Seifenfabrikant 1912, No. 31) furnishes the following data on these products:

	Acid No.	Saponification No.	Unsaponifiable.	Iodine No.
Talgol	3.5	190.7	0.33	63.9
Talgol extra	3.8	190.5	0.31	36.1
Candelite	3.8	190.4	0.41	18.1
Candelite extra	4.4	188.4	0.52	10.4
	Melting Point.	Fatty Acids Titer.	Acid No.	
Talgol	38.5	34.6	199.7	
Talgol extra	45.5	43.5	199.9	
Candelite	48.5	47.4	198.9	
Candelite extra	51.8	50.5	199.9	

Schaal has reported³ the results of his observations on the two products "Talgol" and "Candelite" derived by hydrogenation of train or fish oil, and has called attention to the adaptability of these hardened fats in the production of soap base or milled soap. Both Talgol and Candelite have a tallowy appearance with this difference that one is softer and one is harder than tallow. At first glance one is likely to regard these fats as similar to high grade soap tallow, but the odor of the product immediately shows this is not the case. The odor is not disagreeable and, in fact, resembles some grades of tallow. It is suggestive of the cheesy odor given off by tallow which has been stored for a considerable time in warm weather. Of the two products, Talgol and Candelite, the odor in the latter is less noticeable.

In his first investigations Schaal simply replaced a part of the softer fats as he thought Talgol would lose its firm consistency during the boiling operation, and would return to a consistency approaching that of the original oil. This assumption proved to be unwarranted, as tests with small samples showed that the Talgol fatty acids were as hard as the Talgol itself. The first fat mixture used for preparing a soap consisted of the following:

40 parts tallow.
15 " Talgol.
30 " bone fat.
15 " coconut oil.

No rosin was used as it was desired to determine the influence of the Talgol odor. During the boiling the odor of Talgol was plainly in evidence, much more noticeable, in fact, than could be observed afterwards in the finished soap. The dried curd exhibited a wholly agreeable odor in which the characteristic odor of Talgol could not be detected, and no odor was in evidence of a nature calculated to affect the perfume. The soap was not perfumed, but was wrapped in paper and laid aside a few weeks for further observation. In another trial the tallow was reduced and the Talgol increased in amount, the formula being:

25 parts tallow.
35 " Talgol.
30 " bone fat.
10 " coconut oil.

The saponification progressed satisfactorily, indicating that Talgol readily united with alkali. As the bone fat employed was of exceptionally dark color, the soap was bleached in the kettle with 0.2 per cent Blankit. The dried product had a fine ivory white appearance, but the odor of Talgol was apparent although not so pronounced as to render the soap unusable. This soap base milled very smoothly and easily, giving an excellent finish. In another trial 5 per cent of rosin was introduced with improvement in the odor of the soap base.

The milled and perfumed soap was kept under observation, and it was noted that some perfumes were

affected by the Talgol odor. A person with a keen sense of smell would immediately detect the presence of Talgol. Tests were conducted with a number of perfumes including hyacinth, lilac, rose, patchouly and violet, each cake being separately wrapped in parchment paper.⁴ It was found that the two first mentioned perfumes were more sensitive to the presence of Talgol smell and gave a momentary impression that the soap had become rancid; the rose was slightly affected, while the other samples were not noticeably changed. Schaal reaches the conclusion that the highest grade of toilet soap perfumed with delicate essential oils is affected by the use of Talgol or Candelite and that these hardened oils will not find an application here. Such soaps are, however, sold only to very fastidious trade and require in any case perfumes of the very highest grade. On the other hand, in manufacturing ordinary grades of toilet soap which are, of course, made in enormous quantities, up to about 35 per cent of Talgol or Candelite may be employed advantageously in the fat stock. As regards solubility in water and free lathering properties, Schaal found Talgol or Candelite to afford satisfactory results, the soaps which he prepared forming a lather immediately which was thick and voluminous, acting, in fact, like any standard soap. It is reported that the Olwerke Germania has been successful in producing a completely odorless product at a somewhat higher cost. If such a deodorized product can be put out at reasonable price, it will be possible to make toilet soaps of the highest grade with hardened fats derived from relatively cheap oils.

Of Talgol Schaal notes that the fat is readily deprived of its glycerine and especially well by the Krebitz process, and soaps made from this stock are prime products.

Schaal states that so long as these hardened fats are not entirely odorless, they cannot be advanced for the manufacture of soap stock of the first class. For these, the best beef tallow, etc., must remain the raw material, for this class demands the best that the soap industry can produce. Talgol is, therefore, considered suitable only for working up into soap stock of second and third grade. In these soaps the price of raw material plays a considerable role, and thus Talgol proves an advantageous substitute for tallow.

The U. S. Consul at Amsterdam reports that the manufacture of coloring substances has been initiated in the Amsterdam district, following the advice of an expert who has investigated the subject. To avoid undue risk, the undertaking will begin in a small way on the premises of a chemical factory at Naarden, 10 miles east of Amsterdam. Important users of dyestuffs and dealers in the raw materials thereof offer to assist the new enterprise. It will begin with the production of aniline dyes and enlarge its operations if results justify.

³The result of protracted investigations by Schaal on the utilization of hardened oils in soap manufacture are published in the *Seifenindustrie Zeitung*, 1912, 821, 846, 954 and 979; 1913, 173, and in a book entitled *Die Moderne Toiletseifen-Fabrikation*, Augsburg, 1913.

⁴Schaal gives a number of perfume formulae for hydrogenated oil soaps in *Seifen. Ztg.* 1912, 979.

IRON ORE PRODUCTION IN 1915.

The iron ore mined in the United States in 1915 reached the great total of 55,526,490 gross tons, the greatest output made in any year except 1910 and 1913. The shipments in 1915, namely 55,493,100 gross tons, valued at \$101,288,984, were a little less than the quantity mined. The quantity mined in 1915 was an increase of 14,000,000 tons over the output in 1914. The increases in quantity and in value of iron ore shipped amounted to about 40 and 41 per cent, respectively. The average value per ton in 1915 was \$1.83, compared with \$1.81 in 1914. These figures, which are just made public by the United States Geological Survey, were prepared by E. F. Burchard, who states that the production of iron ore from the Lake Superior district alone in 1916 will possibly be 60,000,000 tons, and that there will probably be an increase in price of 70 to 75 cents a ton for this ore.

Iron Mining by States.—Iron ore was mined in 27 states in 1914 and 23 in 1915. Three of these states, Idaho, Nevada and Utah, produced small quantities of ore for metallurgical flux only; part of the production from California and Colorado was for smelter flux and part for pig iron and ferroalloys; the remaining states produced iron ore for blast furnace use only except small tonnages for paint from Georgia, Michigan, New York, Pennsylvania, and Wisconsin. Five states, Minnesota, Michigan, Alabama, Wisconsin and New York, which have in recent years produced the largest quantities of iron ore, occupy in 1915 their accustomed places. Only one of these states, New York, produced less than 1,000,000 tons in 1915.

IRON ORE MINED IN THE UNITED STATES IN 1914 AND 1915, IN LONG TONS.

State.	1914.	1915.	Per cent of change in 1915.
Minnesota	21,916,901	33,464,660	+52
Michigan	10,796,200	12,514,516	+16
Alabama	4,838,959	5,309,354	+10
Wisconsin	785,512	1,095,388	+24
New York	785,377	998,845	+27
Wyoming	366,962	434,513	+18
New Jersey	350,135	415,234	+19
Pennsylvania	406,326	363,309	-11
Virginia	378,520	348,042	-8
Tennessee	330,214	284,185	-14
Georgia	67,727	115,701	+71
North Carolina	57,067	66,453	+15
Missouri	37,554	40,290	+7
New Mexico	81,380	34,806	-58
Colorado	10,461	*	*
Connecticut	9,149	*	*
Maryland	6,369	5,500	-14
Nevada	*	3,993	*
Massachusetts	7,600	3,950	-48
Ohio	5,138	3,455	-33
California	1,382	646	-50
Kentucky	21,400		-100
West Virginia	6,530		-100
Other states†	40,800	23,650	-69*
	41,439,761	55,526,490	+34

*Less than three producers in Colorado and Connecticut in 1915 and in Nevada in 1914, and permission was not granted to publish State totals. Increases and decreases in 1915, therefore, included in "Others states." †1914: Idaho, Mississippi, Montana, Nevada and Utah; 1915: Colorado, Connecticut, Idaho and Utah.

Iron Mining by Districts.—The principal iron-mining districts in the United States, except the Adirondack district, are interstate, and statistics of production by districts are of more interest and importance than statistics by states. The Lake Superior district mined nearly 85 per cent of the total ore in 1915 and the Birmingham district about 8.5 per cent, or a little more than one-tenth as much as the Lake district. None of the other districts mined as much as 1,000,000 tons. The increase in production in 1915 was especially marked in the Lake Superior district, where it reached 40 per cent; the Adirondack and Chattanooga districts each showed a large increase, namely, 28 and 25 per cent respectively; the total for a number of widely separated districts, including those in the western states, showed a decrease as compared with 1914.

IRON ORE MINED IN THE UNITED STATES BY MINING DISTRICTS IN 1914 AND 1915.

District.	1914.	1915.	Per cent of change in 1915.
Lake Superior*	33,510,403	46,944,254	+40
Birmingham	4,282,556	4,748,929	+11
Chattanooga	432,006	539,024	+25
Adirondack	544,724	699,213	+28
Northern New Jersey and southeastern New York	541,084	644,493	+19
Other districts	2,098,988	1,950,577	-7
	41,439,761	55,526,490	+34

*Includes only those mines in Wisconsin which are in the true Lake Superior district.

Lake Superior Iron Ranges.—All the ranges in the Lake Superior district mined a larger quantity of iron ore in 1915 than in 1914, the largest increases having been in the Mesabi and Cuyuna ranges—56 and 44 per cent respectively. The output of the Cuyuna Range exceeded 1,000,000 tons for the first time.

IRON ORE MINED IN LAKE SUPERIOR RANGES* IN 1914 AND 1915.

Range.	1914.	1915.	Per cent of increase in 1915.
	Gross tons.	Gross tons.	
Marquette (Michigan)	3,320,763	3,817,892	15
Menominee (Michigan and Wisconsin)	3,671,499	4,665,465	27
Gogebic (Michigan and Wisconsin)	4,601,240	4,996,237	9
Vermilion (Minnesota)	1,362,416	1,541,645	13
Mesabi (Minnesota)	19,808,434	30,802,409	56
Cuyuna (Minnesota)	776,051	1,120,606	44
	33,540,403	46,944,254	40

*Includes only such Wisconsin mines as are in the true Lake Superior district.

Consumption of Iron Ore.—The apparent consumption of iron ore, obtained by adding together the shipments of ore from the mines, the sales of zinc residuum, and the imports of iron ore, and deducting from the sum of these the exports of iron ore, was 56,286,058 gross tons in 1915, compared with 40,613,448 gross tons in 1914, an increase of nearly 39 per cent. The ratio of pig iron produced to iron ore consumed was 53.15 per cent in 1915 compared with 57.45 per cent in 1914.

Largest Iron Ore Mines.—There were 7 mines that

produced more than 1,000,000 tons of iron ore each in 1915, 2 more than in 1914. First place in 1915 was held by the Mahoning mine at Hibbing, Minn., second place by the Hull-Rust mine at the same place, and third place by the Red Mountain group near Bessemer, Ala. The production of these mines in 1915 was respectively, 2,311,940 tons, 2,307,195 tons, and 2,138,015 tons, compared with 1,212,287 tons, 458,468 tons, and 2,008,465 tons in 1914. The Red Mountain group was thus the largest producer in 1914. The increase in production of the Hull-Rust is noteworthy—more than 400 per cent; from practically a condition of idleness the Morris within a year yielded 1,167,421 tons, and the Burt moved from 41st place, with a production of about 250,000 tons to 7th place with a production of more than 1,000,000 tons in 1915. These records illustrate the rapidity with which the rate of output of mines in the Lake Superior district may be increased in response to demand. None but open-pit mines could be made to respond to such a degree.

Pig Iron.—The production of pig iron, including ferroalloys, was 29,916,213 gross tons in 1915, compared with 23,332,244 gross tons in 1914, an increase of 28 per cent, according to figures published by the American Iron and Steel Institute, February 26, 1916. The pig iron, exclusive of ferroalloys, sold or used in 1915, according to reports of producers to the United States Geological Survey, was 30,384,486 gross tons, valued at \$401,409,604, a gain of 36 per cent in quantity and 34 per cent in value. The average price per ton at furnaces in 1915 as reported to the Survey was \$13.21, compared with \$13.42 in 1914. At the close of the year, however, prices of pig iron had advanced 35 to 40 per cent.

In the canvass for iron ore statistics in 1915 the State Geological Surveys of Alabama, Maryland, Minnesota, Missouri, New Jersey, North Carolina, Virginia, and Wisconsin, co-operated with the Federal Survey and that of Michigan co-operated in the subject of pig iron.

It is estimated by the Canadian Census and Statistics Office that 18,000 acres were devoted to the growing of sugar-beet roots in Canada in 1915, all in the Province of Ontario, for the manufacture of beet sugar, as compared with 12,100 acres in 1914. The total estimated yield of roots in 1915 was 141,000 tons, compared with 108,600 tons in 1914, the average yield per acre being 7.83 tons, compared with 3.98 tons in 1914. At an average price of \$5.50 per ton, the total value of the crop in 1915 was \$775,500, compared with \$5.00 per ton and a total value of \$651,000 in 1914. The production of refined sugar made from Canadian sugar beets grown in 1915 was returned as 36,838,267 pounds, compared with 27,345,248 pounds in 1914, and 23,964,272 pounds in 1913.

TESTS OF TIN PLATE BATHS.*

By FRANK C. MATHERS and BARRETT W. COCKRUM.

This work was undertaken at the suggestion of Dr. W. D. Bancroft, of Cornell University, who is chairman of a committee appointed by the American Electrochemical Society, in April, 1913, to investigate the problems of electroplating. Attention was directed towards tin on account of the great number of different baths for tin plating and the absence of any bath which is widely accepted by platers as satisfactory. This indicates that the baths, as described, do not produce satisfactory deposits.

The demand for the electro-deposition of tin is very small on account of the easily executed process of tin-coating metals by dipping in molten tin. However, the lack of a really satisfactory plating bath makes the amount of electro-deposition of tin still smaller.

MANIPULATION.

Each of the various tin baths described by Kern¹ in his review upon tin plating was prepared and electrolyzed at 0.4 amp. per sq. dec. (3.6 amp. per sq. ft.) under the prescribed conditions of temperature, acidity, stirring, etc. Two anodes of commercial tin, one on each side of the beaker, were suspended by iron wires in alkaline baths, by lead wires in complex baths where anode corrosion was good, and by platinum wires in the others. The baths were stirred occasionally with glass rods during the course of the electrolysis. The cathodes were of iron or thinly rolled pure tin. In each case electrolysis was continued constantly for two weeks, the cathodes being replaced by new ones whenever crystalline or spongy growths seemed to produce short-circuits.

CLASSIFICATION OF TIN BATHS.

The baths for tin plating seem to fall into three principal classes, as follows:

1. Tin salts of mineral acids, with or without other inorganic salts or organic addition agents.
2. Alkaline baths, as sodium stannite, with or without other salts.
3. Complex or double salts.
4. Alkaline sulphides.

These latter were not tried in this work.

TIN SALTS OF MINERAL ACIDS.

Many of the difficulties in tin plating are unavoidable because they lie in the specific inherent properties of tin salts and in the pronounced tendency of metallic tin to be electro-deposited in a loosely crystalline or a spongy condition. Stannous salts easily oxidize in the air with the formation of basic insoluble compounds, unless an excess of strong acid is present. The sulphate, being almost insoluble, and the nitrate,

*Paper presented at the 29th General Meeting of the American Electrochemical Society, Washington, D. C., April 27-29, 1916.

¹Trans. Am. Electrochem. Soc., 23, 199 (1913).

being unstable, cannot be used. This leaves, among the cheaper salts, only the chloride or the fluoride and no advantage seems to lie in the use of the more troublesome fluoride. A bath of stannic salts is reduced at the cathode by the current and a constant deposition of tin is not attained until a certain ratio of stannous to stannic salt is present, which ratio is theoretically the same as the ultimate composition of a bath made from stannous salts. Hence a solution of stannous chloride containing hydrochloric acid and perhaps such other salts as sodium chloride, ammonium chloride, etc., is the simplest and cheapest bath. Hydrofluoric, perchloric, fluoboric, and fluosilicic acids give soluble stannous salts, and they could be used for plating if they gave satisfactory deposits, although they are more expensive. An extensive study² has already been made in this laboratory of baths containing many combinations of tin salts of the mineral acids, both with and without organic addition agents, but in no case was it found possible to obtain a solid, firm deposit that was free from coarse or rough crystals. The deposits were masses of right glistening crystals which adhered fairly well in some cases. This class of baths is of no value where a solid, uniform deposit is desired, a fact that seems generally recognized, as is shown by the absence of baths of this kind among those recommended for plating purposes.

ALKALINE BATHS.

Tin salts readily dissolve in an excess of sodium hydroxide, forming a clear solution which remains free from precipitate and which would be satisfactory as the basis of a plating solution if such baths yielded firm, solid deposits. The voltage required by these baths is high, and the anode corrosion is low in many of them. A very large proportion of the tin baths which have been recommended for plating belong to this class, which may be further divided as follows:

(a) *Sodium stannite or potassium stannite, without the addition of other salts.* The baths³ which were tried contained from 1.2 to 1.4 per cent of tin as stannous chloride and from "sufficient alkali for a clear solution" up to 6 per cent of potassium or sodium hydroxide. In all cases the deposits were masses of small, bright crystals which were worthless as a protective coating.

(b) *Sodium or potassium stannite and tartrates.* The addition of tartrates⁴ to the alkali stannite baths did not improve the character of the deposit, which was spongy from the bath containing only 1.3 grams of fused stannous chloride per liter but crystalline from the bath containing 3 grams of the same salt per liter.

(c) *Sodium or potassium stannite and potassium*

cyanide, with or without other salts. The various baths⁵ are as follows:

Baths 11, 12, 13, 14, 15 and 16 in Kern's Report.	Loc. cit.	
KCN.	K ₂ CO ₃ or Na ₂ CO ₃ (cryst.).	KOH or NaOH.
10	82.5	5.5
11	11	to
1	80	dissolve
10	110	2.5
111	1.2	7.5
35	7.5	111

None of these gave good deposits of any considerable thickness. The following general observations were made:

1. With large amounts of carbonate and little or no sodium hydroxide, the anodes dissolved so poorly that the tin in the bath was soon exhausted, after which both electrodes gassed vigorously. These baths gave good looking, bright deposits which were very thin, however. The current yields were very low, as was indicated by the quantity of gas evolved at the electrodes. It would require an extremely long time to obtain a deposit of any reasonable thickness from such a bath.

2. Potassium cyanide seemed to be without much influence upon the crystalline structure of the cathode.

3. Very large amounts of the potassium cyanide must be accompanied by correspondingly large amounts of sodium hydroxide, otherwise the tin is precipitated as a sludge in the bath and, upon electrolysis, little tin is deposited upon the cathode.

A bath containing 9 per cent potassium hydroxide, 0.35 per cent potassium cyanide, 0.75 per cent potassium bitartrate, and 0.75 stannous chloride is used commercially⁶ in barrel plating. The bath is run hot (70° C.) and a thin deposit is obtained. At intervals more of the potassium cyanide must be added. Experiments with this bath in a still solution indicated that thick deposits could not be obtained because of the formation of projecting crystals. However, very thin deposits appeared to be good, because the crystals were too small to be readily seen. The tumbling in the barrel would compact the deposit into a more firm and solid coating.

(d) *Sodium stannite and sodium thiosulphate.* The baths⁷ contained, in per cent, as follows:

Baths 17, 18 and 19 in Kern's Report.	Loc. cit.	
Na ₂ S ₂ O ₃	NaOH	SnCl ₂
7.5	12.5	5
6	12	3
1.5	9	3

The baths with 6 per cent or more of the sodium thiosulphate gave firm, finely-crystalline deposits, which became rough on continued electrolysis. A fine black precipitate was formed in the bath when the sodium thiosulphate was added. The deposits from these baths were the best obtained from any bath described by Kern. The deposits were dark but became bright and metallic after buffing. On continued electrolysis the deposits became rough and nodular, but projecting roughly adhering crystals were absent. Solutions at room temperature worked better than at 60° C. (140° F.). The voltage was 1.2.

²Mathers and Cockrum, Trans. Am. Electrochem. Soc., 26, 133 (1914).

³Baths Nos. 6, 7 and 8 in Kern's Report. Loc. cit.

⁴Baths 9 and 10 in Kern's Report. Loc. cit.

⁵Private communication.

COMPLEX OF DOUBLE SALTS.

(a) *Pyrophosphates*. The Roessler bath,⁸ or modifications of it containing 1 to 3.7 per cent of sodium pyrophosphate and 0.1 to 2 per cent of fused stannous chloride, is highly recommended by various writers. The deposit from a hot solution is said to resemble silver. We are aware that this bath is used commercially, but nevertheless the deposits in our experiments were spongy and non-adherent. It seems that only thin deposits are produced, and that tumbling or scratch-brushing must be resorted to in order to give the deposits a bright, metallic appearance. Two of these baths, which are used commercially,⁹ are:

1. Six parts of sodium pyrophosphate to 1 part of fused stannous chloride. It is said that the concentration can vary within rather wide limits without affecting the deposit very much.

2. Three per cent sodium pyrophosphate, 0.75 per cent fused stannous chloride and 0.2 per cent alum.

It is claimed that these baths may be run either hot or cold, but that only a low current must be used. It is recommended that a saturated solution of fused stannous chloride in sodium pyrophosphate be added at intervals to compensate for poor anode corrosion.

(b) *Stannous Ammonium Oxalate*. A deposit consisting of long, needle-like crystals was obtained from a bath⁹ containing 2 to 3 per cent stannous chloride, 5.5 to 6.5 per cent ammonium oxalate and 0.3 to 0.4 per cent oxalic acid. The completed bath was heated to boiling before using. The addition of peptone¹⁰ to a modification of this bath containing more tin, prevented the formation of loose crystals and produced by far the smoothest, firmest and thickest deposit of tin which was obtained from any tin bath.

(c) *Acid Tartrate*. A bath¹¹ containing 6 per cent potassium hydrogen tartrate and 1.5 per cent stannous chloride gave a mass of small, loosely adherent crystals. After two weeks of continuous electrolysis, the crystals became much smaller and showed a tendency towards sponginess. The anodes dissolved unevenly.

The various dip or immersion solutions for tinning by contact without the use of outside current gave bright deposits of tin, thereby confirming all that is said of them in the literature and in the books upon plating.

SUMMARY.

The various baths for tin plating, which were described by Kern,¹ were prepared and electrolyzed for two weeks with a current density of 0.4 amp. per sq. dec. (3.6 per sq. ft.) under the conditions recommended.

In no case was a satisfactory deposit obtained, although the sponsors for the various formulas have made roseate claims for them. In most cases the

deposits were masses of more or less adherent crystals, although in some cases they were spongy.

Among the baths described by Kern, the Bencker bath¹² containing 25 gms. of sodium hydroxide, 10 gms. stannous chloride and 15 gms. of sodium thiosulphate in 200 cc. of water, gave the smoothest, firmest deposits of good thickness. The deposits were dark in color but could be scratch-brushed to a bright, metallic appearance. The bath seemed to gradually deteriorate, the deposit becoming black and at last non-adherent. This bath is considered to be far below the quality desired for electroplating.

Some of the baths containing combinations of potassium cyanide and alkali carbonates or hydroxides with a little stannous chloride gave bright deposits, but there was a simultaneous liberation of hydrogen, and anode corrosion was poor. Such thin flashings hardly deserve the name of tin plating.

The stannous ammonium oxalate bath containing peptone as an addition agent¹⁰ gave a smooth, firm, finely-crystalline deposit, the best obtained from any bath.

The production of coal in Utah in 1915 amounted to 3,108,715 short tons, valued at \$4,916,916, an increase of 5,679 tons in quantity and a decrease of \$18,538 in value, as compared with 1914, according to the United States Geological Survey. The principal gain was in Emery County, and there was a small increase in Carbon County. The production of Summit and Uinta counties decreased more than 30,000 tons. The number of employes decreased from 4,112 in 1914 to 3,564 in 1915, and the average number of days worked decreased from 210 to 208. The average annual output of coal per employe increased, however from 755 to 872 tons, and the average per day from 3.6 to 4.2 tons, a high average. Machine mining has increased greatly in Utah in recent years, the returns showing 20 per cent in 1913, of the total product mined by that method, 30 per cent in 1914, and 50 per cent in 1915.

According to British reports steel and pig iron production in Germany shows a continued expansion of output. The steel ingot outputs for February and March were 1,236,845 and 1,361,365 metric tons respectively, against 1,227,120 tons in January. The daily output was 40,473 tons in February and 50,421 tons in March; in March, 1915, it was 40,677 tons. The steel production in March, 1914, before the war, was 1,634,297 tons or 62,857 tons per day. The following table shows the grades of steel made in February and March this year, in metric tons:

	February, 1916.	March, 1916.
Bessemer steel.....	602,543	664,730
Open-hearth steel.....	535,113	584,920
Steel castings.....	76,774	85,850
Crucible steel.....	8,564	9,773
Electric steel.....	13,851	16,092
Total	1,236,845	1,361,365

¹²U. S. P. 921,943; Met. Chem. Eng., 7, 285 (1909).

⁸Bath 2 in Kern's Report. Loc. cit.

⁹Bath 1 in Kern's Report. Loc. cit.

¹⁰See Mathers and Cockrum: Trans. Am. Electrochemical Soc., 29, — (1916).

¹¹Bath 5 in Kern's Report. Loc. cit.

A COMPARATIVE COLOR PHOTOMETER.*

By ARTHUR HOWLAND.

The photometer is essentially a light tight box with a slide in the front having a small opening through the aperture of which the operator sees the absolute black of the interior. It contains a small high speed motor with a shaft arranged for clamping discs of paper or thin cardboard, which may be spun close behind the opening. The motor is screened from view by a second partition covered with black velvet, while a third screen back of the motor aids in absorbing any light rays which might otherwise find

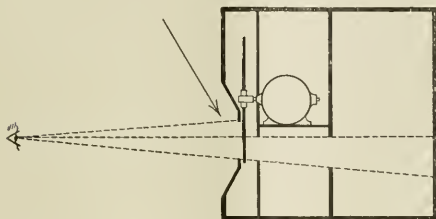


Fig. 1.

their way to the black velvet which covers the back of the box on the inside. By this method the background is so completely screened that the effect on looking into the opening is one of absolute black. In operation, the machine should be so set up that light will enter only in the direction indicated by the arrow in Fig. 1, while the operator should stand directly in front of the box with his eye at the level of the opening and about fifteen feet away.

Sectors of all sizes from 0 to 100 percent similar to those shown in Fig. 2, are provided, with ends carefully coated with magnesium carbonate. Colored sectors of the same pattern are furnished in a few of the strongest colors obtainable.

With this outfit it is then possible to produce practically all known colors in every conceivable strength or luminosity. Mixing a white sector with the black of space gives an absolutely pure neutral gray of any desired luminosity as set by the size of the sector chosen, from a blacker black than any known pigment, to a purer white than has ever been produced in papers or pigments.

Mixing a colored sector with the black of space, gives the deeper shades of the same color or by using the white sectors in conjunction with the colored ones it is possible to make grayer or lighter tones of the same color. Again, by combining any two of the colors provided, in this same way it is a simple matter to produce any color desired within the limits set by the strength of the working colors used. To make the machine of practical value, it is necessary to discover very strong and pure colors.

Also it is quite essential that the colors be laid upon the sectors with an absolutely colorless medium

as any oil or varnish vehicle would tend to discolor them to a marked degree.

After fully two years of research work such colors have been obtained and a method of applying them to fine white card stock has also been found. If at any time stronger colors are discovered they will simply increase the range of usefulness of the apparatus to within their own limits of strength.

Since all possible combinations of color may be made with this photometer, it is practically an easy matter to study the geometrical relationship of pigment colors with a view to charting them for commercial as well as educational purposes. Incidentally it has been found practical to place them with such accuracy that all combinations may be figured mathematically by using the three properties of color, hue, strength, luminosity.

THE CHART.

The photometer is best used in conjunction with a chart which might well be called a "colorless" color chart (see Fig. 5) since there are absolutely no colors upon it, although every point of its entire surface may represent a different color or varying luminosities of the same color for any one spot.

It has long been known that every color has its opposite or "complementary" color, the combination of which will always give gray if spun in the proper proportions for exact neutralization.

By imagining each color as projected down upon a horizontal plane, we are enabled to use ratios of distances between them just as easily as if it were pos-

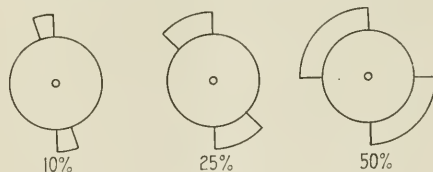


Fig. 2.

sible to take the measure of the actual distances in space. To illustrate: If R (Fig. 3) is a certain red situated above a given plane and R' is its projection upon that plane, and if G and G' are respectively the position and the projection of a certain green, then if we wish to make a color Y intermediate between R and G, it is only necessary to spin the red and green discs together in the ratio of a' parts of red to b' parts of green to get the resultant color Y, which in this case is a dull yellow, since a' is to b' as a is to b. (In this case 3 to 5.) Suppose that our red has a luminosity of 27 percent of that of our standard white and that the green has a luminosity of 25 percent, then to figure the resultant color, we use the following form:

Area	Luminosity
R 37.5 per cent.....	.10125
G 62.5 per cent.....	.15625
	.25750

*From Science Conspectus.

This means that the resultant color, yellow, has a luminosity of 25.75 percent if made from the red and green above mentioned.

To produce this result the discs should be set as shown in Fig. 4.

All known colors may be placed about a neutral axis in space and will actually respond with mathematically exact spinning ratios to the above method of procedure, provided they be properly located in their true positions according to their three properties of hue, strength and luminosity. By knowing the luminosity of the comparatively few working colors on the prepared discs and sectors, it is a very easy matter to figure out beforehand what color will result from any possible combination.

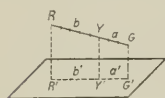


Fig 3



Fig 4



Fig 6

Figs. 3, 4 and 6.

As there are endless combinations that can be made, it is also possible to figure combinations of other colors that will produce identically the same resultant and the color photometer will actually permit of making both at the same time. For an example, take the above red and green in the proportions given to make a dull yellow. At the same time spin sectors of a strong yellow and white (with the black of space) on the same shaft with the red and green. (Fig. 6.)

If the proportions of all of these colors used are taken from the horizontal chart as figured from the point where the lines between the components cross, it is an easy matter to figure both sets with such accuracy that the two combinations will match absolutely even though it may never have been done before.

If a strong yellow Y (Fig. 5) has a luminosity of 80 percent and the chart shows a ratio to the meeting point Y' of say 18 percent of the yellow to 82 percent of neutral gray N (black and white) the equation would stand as follows:

$$\begin{array}{rcl} R \text{ 37.5 per cent...} & .10125 & \\ G \text{ 62.5 per cent...} & .15625 & \\ \hline & .25750 & \end{array} \quad \text{equals} \quad \begin{array}{rcl} \{ Y \text{ 18 per cent...} & .1440 & \\ \{ N \text{ 82 per cent...} & .1135 & \\ \hline & .2575 & \end{array}$$

The diagram Fig. 5 represents the "plan view" of an imaginary color solid containing within its limits practically every known pigment color. The reader may be considered as above the drawing looking down upon the highest point of the solid at N, which point represents the upper or white end of the neutral axis containing all possible grays from absolute black to white. The lower or black end rests upon the plane of the paper.

Each of the limiting points of the diagram may be considered as the projection upon the plane, of various

colors of great strength whose hues vary with their angular positions about N in exact accordance with the order of the spectrum through red, orange, yellow, green, blue, violet, and whose positions above the paper are fixed by their respective luminosities. Their relative strength is indicated by their distances from point N radially outward as 10, 20, 30, etc., and is determined by the concentric circles. Note that between the blues and the reds will be found all purples which are seen only in spectral colors when spectra overlap, the violet end of one with the red end of another.

While the placing of colors upon a chart in this manner is purely an imaginary one, it is nevertheless a fact that when properly placed they will respond with marvellous accuracy to exact laws of combination which this figure portrays. As soon as three color points have been determined, all other colors must then occupy fixed positions with respect to them.

Such colors will then obey the law of moments of forces with mathematical accuracy where the spinning area times the strength of one will always equal

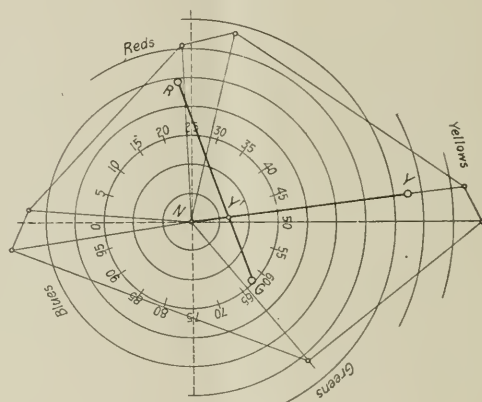


Fig. 5.

the spinning area times the strength of the other when opposed to each other as complements.

Moreover, when once a few strong colors have been properly located upon this chart, it is then possible to figure in color and solve problems mathematically, predicting the exact resultant color in all three of its properties of hue, strength and luminosity.

It will be noticed that the diagram is very nearly a true parallelogram, with the four colors red, yellow, green and purple-blue at the four corners. It should, then, be possible to produce all colors lying within these bounding points from a combination of these four with black and white. That such is actually the case may be most beautifully demonstrated by the use of four such powerful working colors in the photometer described above.

Therefore the colors Y' would be identical, since

their position on the chart indicates their similarity of both hue and strength, and their luminosities are both .2575 as compared with the same standard.

These, of course, are very simple examples of what may be done with the machine in an educational way, but they lead to very remarkable possibilities with the refinements that are bound to come in the future.

It is always possible to retain a sample of the working colors in the dry powder form, which if kept in the dark in glass containers will not fade or change in any manner, so that they will always give a standard with which to work. If, then, a color is once matched to the standard *made from these working colors*, it is always possible to produce again the same standard from these working colors by taking some of the dry color which has been kept under proper conditions and placing it upon fresh discs and sectors. Manufacturers abroad could have working colors from the same pigments as standards and could reproduce any point upon the chart that might be indicated by American distributors. Such points could be indicated in several ways with great accuracy. While the actual percentage of each working color used in any given case might be easily cabled, a better way would be to designate each color wanted by three numbers indicating in order, the hue, the strength and the luminosity.

The three numbers, 23-49-31, for instance, stand for one color only, namely a red R (Fig. 5) whose hue is 23 percent of the angular distance from a point of lowest luminosity in the circle of spectral hues taken as 0, whose strength is represented by 49 units of distance out from the neutral point N, and whose luminosity is taken from comparison with the standard white used and is found to be 31 percent.

An American manufacturer can match a piece of goods to his combination of sectors, locate it upon his own chart and cable the result to Paris or London, to any house that has a similar outfit with the certainty that under the same lighting conditions an absolute match will be obtained. Under ordinary conditions daylight from a north skylight will give satisfactory results but for very accurate matching it will be found that it is better to do the work by the aid of an incandescent lamp outfit with a screen and voltage regulator similar to some of those now upon the market for this very purpose.

Educationally, the photometer should be a wonderful aid to teachers and supervisors, who would be able to illustrate to their classes the exact composition of any given color, the relation of one color to any other, the harmony of different hues of the spectral circle, the complete separation of luminosity from hue or strength, and last, but not least, the fascinating process of producing new colors that have never been equaled in pigments. The machine is so sensitive that it will analyze even a black pigment, showing with great accuracy the percentage of red, or blue or green that is in it and making it possible to correct it to a completely neutral black.

There is probably no manufacturing process today that does not use color in some form and it will undoubtedly be used even more generally in the future when some such standard will come into general use throughout the civilized world.

STATEMENT OF FLOTATION OILS.*

By O. C. RALSTON.

MARKET SITUATION REGARDING FLOTATION OILS.

The sudden development of the art of flotation has brought about peculiar conditions in the oil market. A few years ago there was considerable expansion in the wood-distilling industry throughout the South on the hope of selling turpentine at not less than 50 cents per gallon. This hope was never realized and the industry became demoralized owing to excessive production and the efforts of some plants to keep going even at a loss. Pine oil, which previously has had little sale, is a by-product from this industry and has been found one of the best oils for flotation purposes. At the time of the introduction of the flotation process into the country a stock of pine oil that had accumulated was for sale at an attractive figure.

This supply of pine oil and its derivatives has been largely exhausted and we are having to depend upon current production for the present supply. Hence the price has soared, and some of the pine oil on the market has been adulterated. Pine oil is also proving to be a valuable antiseptic and it is doubtful whether it will never again be sold cheaply. Furthermore, turpentine is now about 50 cents per gallon and the fractionation of the wood distillate is being made in favor of a high yield of turpine.

During 1915 the principal investigation in connection with the flotation oils was conducted for the purpose of finding a substitute for pine oil now costly. Most of the wood creosotes have proved acceptable and are now being sold at lower prices than the pine oils. How long this condition will continue is a matter of conjecture. The creosotes have proved to be good preservatives of wood, especially of railroad ties. However, coal creosotes excel wood creosotes for preserving timber, so that flotation will probably cause most of the wood creosote to be diverted from timber preservation. Further, the starting of many large flotation mills during the coming year, and the enlargement of many that have been operating in an experimental way, may create such a demand for wood creosote that the cost of this oil may equal that of pine oil.

In view of such a possibility, considerable work has been done to determine whether coal tar and coal tar creosote could not be successfully used as flotation oils. In many instances it was possible to do so only after adding a small amount of one of the true wood oil. There is some difficulty in getting the thick,

*Issued by Bureau of Mines, Department of Interior.

heavy coal tar to mix well with the pulp, so that it is not the most desirable medium, and for that reason the coal creosotes have met with more favor. Consequently, most of the gas plants throughout the country have been able to contract for their output of creosote for some time to come. A similar condition prevails with regard to most of the wood oils. There has been somewhat of a rush in the mining industry for contracts for these products in order that proposed mills will be assured of being able to operate. When Germany gets into the coal creosote market again there will doubtless be lower prices for that particular product.

The petroleum men have not been slow to seek the flotation oil market but their products have not as yet met with much success when used alone. It is possible to mix small amounts of pine oil or creosote with various petroleum products such as stove oil and to obtain flotation with some degree of success, but the general tendency of petroleum products is to float both gangue and mineral non-selectively. The petroleum products that have met with the most success are some of the crude oils, such as Texas crude, and especially certain high-sulphur crude petroleum, obtainable in Kansas and in California. "Stove oil" has met with some success in the copper-concentrating mills, as copper minerals do not have to be concentrated to the same degree of purity as do the lead and zinc minerals. It is probable that, for the wood oils, the copper mills will be able to use cheaper substitutes, such as petroleum products, than will the mills treating base metals.

One other product that has met success has been the "kerosene acid sludge" from certain of the petroleum refineries. This material is the resultant of the removal of certain impurities with sulphuric acid and often consists of as much as 50 per cent sulphuric acid. Not all of the acid sludge products have proven suitable, only the California sludge being sold at present.

Just how far all this substitution will be successful is not known and there is no way to predict. The test work of the coming year should go far towards solving this problem.

PRODUCERS OF OILS MORE OR LESS ADAPTED TO FLotation.

Following is a list of dealers in different oils who have placed on the market various products. A host of these dealers are prepared to supply these products at any time, and of fairly uniform quality. None of them has been able to exactly duplicate their carload shipments, so that the general practice is to test each shipment of oil in a laboratory testing device to determine the proper method of using a given shipment of oil. This non-uniformity of shipments will doubtless vanish when the market becomes steady.

DEALERS IN FLotation OILS.

WOOD OILS.

1. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Pensacola Tar & Turpentine Co., Gull Point, Fla.
2. Pine oils, rosin oils, wood creosotes, tar oils, turpentine,

etc.—General Naval Stores Co., New York.

3. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Georgia Pine & Turpentine Co., 138 Perry St., New York.
4. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Central Distilling Co., Helena, Ark.
5. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—United Naval Stores Co., Helena, N. Y.
6. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—American Tar & Turpentine Co., New Orleans, La.
7. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Cleveland Cliffs Iron Co., Cleveland, Ohio.
8. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Chesapeake Tar & Rosin Co., Baltimore, Md.
9. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Custer City Chemical Co., Custer City, Pa.
10. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Yarvan Naval Stores Co., Brunswick, Ga.
11. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Hussay & O'Connell, Savannah, Ga.
12. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Florida Wood Products Co., Jacksonville, Fla.
13. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Oregon Wood Distilling Co., Portland, Ore.
14. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—National Wood Products Co., Wilmington, N. C.
15. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Chapman Manufacturing Co., Savannah, Ga.
16. Pine oils, rosin oils, wood creosotes, tar oils, turpentine, etc.—Spirite Chemical Co., Wilmington, N. C.
17. Eucalyptus oil—Atkins Kroll & Co., San Francisco, Cal. And other importers.

COAL TAR, COAL CREOSOTES, AND AROMATIC HYDROCARBONS.

1. The Barrett Co., New York.
2. F. J. Lewis Manufacturing Co., Chicago, Ill.
3. American Creosoting Co., New Orleans, La.
4. American Tar Products Co., Chicago, Ill., and St. Louis, Mo.
5. Republic Creosoting Co., Indianapolis, Ind., and Minneapolis, Minn.
6. American Coal Refining Co., Denver, Colo.
7. Numerous municipal and similar coal-gas plants.
8. Numerous by-product coke ovens, such as:
 - Pennsylvania Steel Co., Steelton, Pa.
 - National Tube Co., Penwood, W. Va.
 - Milwaukee Coke & Gas Co., Milwaukee, Wis.
 - Pennsylvania Steel Co., Lebanon, Pa.
 - Solvay Process Co., Syracuse, N. Y.
 - By-Products Coke Corporation, South Chicago, Ill.
 - Sennett-Solvay Co., Detroit, Mich.
 - Central Iron & Coal Co., Tuscaloosa, Ala.
 - New England Gas & Coke Co., Everett, Mass.
 - Illinois Steel Co., Joliet, Ill.
 - Maryland Steel Co., Sparrows Point, Md.

VEGETABLE OILS.

1. Cottonseed oil, etc.—Southern Cottonseed Oil Co., New York.
2. Corn oil—Corn Products Company, New York.
3. Palm oil—Peter van Schaack & Co., Chicago, Ill.

ANIMAL OILS (FATTY ACIDS).

1. Oleic acid—Peter van Schaack & Co., Chicago, Ill.
2. Oil flotation grease emulsion—Mohawk Refining Co., Cleveland, Ohio.

PETROLEUM PRODUCTS (CRUDE, ASPHALTUM BASE).

1. California crude: Union Oil Co., Santa Paula, Cal. Association Oil Co., Los Angeles, Cal. Standard Oil Co., Richmond, Cal.
2. Road Oil No. 80—Harris Oil Co., Los Angeles, Cal.

RECONSTRUCTED PETROLEUM OILS.

1. Special mineral separator—Continental Oil Co., Salt Lake City, Utah.
2. Solulene and minolene—Star Lubricating Co., Salt Lake City, Utah.

REFINED PETROLEUM PRODUCTS.

1. Stove oil—Standard Oil Co., San Francisco, Cal.
2. Stanolind, etc.—Continental Oil Co., Salt Lake City, Utah.
3. Flotation oils—Utah Oil Refining Co., Salt Lake City, Utah.
4. Heavy mineral flotation oils—Geo. P. Jones & Co., St. Louis, Mo.
5. Refinery acid sludge—Any refinery.
6. Lubricating oils—Any company.

SPECIAL MIXTURES OF MINERAL AND WOOD OILS.

1. Calol oils—Standard Oil Co., Richmond, Cal.
2. Mine & Smelter Supply Co., Denver, Colo.
3. Hendrie Bothoff Manufacturing & Supply Co., Denver, Colo.

COSTS OF FLOTATION OILS.

The costs of flotation oils have varied so much, owing to the unsettled market that it is almost impossible to give an idea of what they should cost. For a rough estimate it is possible to say that crude petroleum will cost the same as for other purposes. Many of the specialized products such as coal tar listed above will cost about 5 cents or less per gallon. The coal creosotes and the wood creosotes cost 15 to 30 cents per gallon; the pine oils 45 to 60 cents per gallon, and eucalyptus oil will cost \$1.50 or more per gallon. The effect of the ending of the war as regards coal tar and creosote in the American market is uncertain but, so far as known, wood products will not be affected, and petroleum products for flotation will almost certainly be little affected. Flotation men do not like to have their oil costs go over 5 cents per ton of slimes treated, and many costs are nearer to 2 cents, or possibly even less.

OILS ADAPTED TO CERTAIN ORES.

There can be no doubt that the higher grade pine oils and other wood oils are the best adapted to general flotation work but the question of what is com-

CONSUMPTION OF FLOTATION OILS.

Table I shows the amount of flotation oils being consumed every month throughout the United States. These figures were collected at the beginning of 1916 by direct communication with the companies. The tonnage of ore being treated was also estimated, and proposed increases allowed an estimate of the probable tonnage by the end of 1916. Owing to the fact that some of the companies were secretive, on account of the litigation situation, the figures are probably in error as much as 20 per cent in either direction and can probably be made more accurate as time goes on.

The products called "Pine oil" probably includes a considerable amount of the lighter fractions of pine tar oil.

The U. S. Geological Survey reports that there was a marked increase in the use of petroleum as a locomotive fuel by the railroads of the United States in 1915. The quantity of oil fuel so consumed last year was 36,648,466 barrels, an increase of 5,555,200 barrels, or 18 per cent over the similar consumption in 1914.

TABLE I.—MONTHLY CONSUMPTION OF FLOTATION OILS IN UNITED STATES.
 Monthly tonnage of ore. ——— Monthly consumption of flotation oils, beginning of 1916, pounds. ———
 ——— Wood products. ——— Coal products. ——— Petroleum. ———

Type of Ore.	Beginning 1916. (Tons.)	End of 1916, estimated. (Tons.)	Pine oil.	Pine Tar oil.	Eucalyptus.	Creosote.	Turpentine.	Oleic acid.	Tar.	Creosote.	Cresol.	Crude.	Fractions.
Copper	1,248,000	1,942,000	59,300	750	...	417,000	1,500	...	677,000	403,000	8,340	79,000	1,702,000
Zinc and complex....	248,000	350,000	60,750	667	...	262,500	3,330	5,830	10,670	46,500	...	157,000	41,000
Lead	115,000	136,000	3,900	...	216	121,000	...	...	9,250	...	...	...	660
Gold and silver	45,700	123,000	9,830	750	...	40,250	...	...	27,450	4,920	...	7,090	6,250
	1,656,700	2,551,000	133,780	2,167	216	840,750	4,830	5,830	715,120	463,670	8,340	243,090	1,749,910

mercially feasible is entirely different. Thus, the wood creosotes are meeting much favor. Many of the special petroleum product, especially those high in sulphur, are adaptable for rough concentration of copper ores, but the most favored materials for such ores at present seem to be the coal-tar products in combination with topped crude petroleum, oils from which the lighter fractions have been removed by distillation. Coal tars and creosotes, with a small addition of pine oils, are being used a great deal in zinc work, and the wood creosotes find favor in the treatment of galena ores. Gold and silver ores seem to require much pine oil although the pine oil can be diluted with some of the coal creosote oils.

It will be found that there is a considerable number of oils that will give good results on any given ore, if the mechanical treatment is adjusted to suit each given oil. The selection of the proper oil in any case is purely a matter of experiment. Local conditions, such as transportation, also influence considerably the choice of oils.

The silica (quartz) sold in 1915 for pottery, tile, glazes, paints, wood-filler, wood-polish, abrasive soaps, fine filters, and other uses, as reported to the U. S. Geological Survey, amounted to 243,340 short tons, valued at \$1,270,835. This product was obtained from quartz veins, pegmatites, quartzites, sandstones, sand, tripoli, and diatomaceous earth in Arizona, California, Connecticut, Illinois, Maine, Maryland, Massachusetts, Michigan, Missouri, Nevada, New Hampshire, New York, North Carolina, Oregon, Pennsylvania, Tennessee, Virginia, and Wisconsin.

In 1915 there were produced in South Carolina 183.29 ounces of gold and 8 ounces of silver, whose total value was \$3,793. The placer mines produced 11.99 ounces of gold and the deep mines 171.30 ounces of gold and all the silver. The average yield of the siliceous gold ores and auriferous pyrite mined in 1915 was 70 cents a ton. The gold quartz ores yielded approximately \$15 a ton. This is the smallest production recorded for South Carolina since 1905.

NITROGEN IN TANNING MATERIALS.*

By HUGH GARNER BENNETT, M.Sc., F.C.S.

As a side issue in certain other investigations, the author was in need of information as to the amount of nitrogenous matters in the common tanning materials. Little information upon this point was obtainable from the usual books of reference, and in consequence, nitrogen determinations have been made with these materials.

The more commonly employed tanning materials were found to exhibit considerable differences in their nitrogen content, varying from one to about twelve parts nitrogen per thousand. It was also observed that the nitrogen content of a tanning material is characteristic of that material, in the same sense as the tannin content is characteristic, *i. e.*, the percentage of nitrogen in any material is not constant, but is approximately so within limits. Hence the nitrogen content supplies another criterion for the identification of a tanning material. The results in the following table are to some extent typical of the materials in question.

Tanning material	cc. N/10 acid per 1 gm. material		cc. N/10 acid per 1 gm. tan.		Mgms. N per 1 gm. tannin	
	% N		% N		% N	
Myrobalans	4.0	0.56	12.9	18.1	12.9	18.1
Valonia (cup)	2.05	0.29	7.4	10.4	7.4	10.4
Valonia (beard)	2.45	0.34	6.4	9.0	6.4	9.0
Natal bark	6.2	0.87	19.2	26.8	19.2	26.8
Sumac	6.2	0.87	25.1	35.2	25.1	35.2
Lentisco	8.1	1.18	49.4	69.2	49.4	69.2
Quebracho wood	1.2	0.17	6.0	8.4	6.0	8.4

It being improbable that all the nitrogen would be extracted from these materials in leaching, it was thought of interest to make nitrogen determinations of various extracts. The percentage of nitrogen in an extract is a figure of little interest or significance, being dependent upon the degree of concentration to which the extract has been subjected, *e. g.*, whether the extract be liquid or solid. If, however, results be calculated as nitrogen per unit tannin, they at once become significant and to a large extent characteristic of the extracts in question. The results may be usefully stated as "milligrams nitrogen per gram of tannin," which results may be called for convenience the "nitrogen value" of the extract.

The nitrogen values of extracts—like the percentage nitrogen in dry materials—are approximately constant and characteristic of the particular materials. Quebracho extracts, for example, have nitrogen values ranging from 1.9 to 2.6, with an average of 2.3. By reference to the results with quebracho wood, it will be observed that about 27 per cent of the nitrogen is leached out in extract manufacture. Myrobalans extract has an average nitrogen value of 8.2,—45 per cent of the nitrogen of myrobalans being leached out.

It will be clear that in these nitrogen values we have also a criterion for determining the composition of

mixed extracts. Blended extracts, for example, made from quebracho and myrobalans, will have a nitrogen value between 2.3 and 8.2, according to the proportions of the two ingredients.

If per cent of myrobalans = x and nitrogen value of mixed extract = N ; then,

$$8.2x + 2.3(100 - x) \times 100N$$

Hence, in the mixed extract of this description recorded in the following table:

$$8.2x + 2.3(100 - x) = 100 \times 4.3$$

$$\therefore x = 34 \text{ per cent.}$$

Of course this is an approximation only, as the nitrogen values of pure extracts vary to some extent. Still this mode of procedure is capable in some cases of yielding useful information.

Some typical results for various extracts are as follows:

Extract	cc. N/10 acid per gm. material		cc. N/10 acid per 1 gm. tan.		Mgms. N per 1 gm. tan.	
	% N		% N		% N	
Quebracho (solid)	0.90	0.126	1.4	1.9	1.4	1.9
" liquid 1	0.75	0.105	1.8	2.5	1.8	2.5
" liquid 2	0.57	0.080	1.9	2.6	1.9	2.6
" (bleach) 2	0.63	0.088	1.6	2.2	1.6	2.2
" (bleach) 3	0.66	0.092	1.7	2.4	1.7	2.4
" (mean :—)	—	—	—	2.3	—	2.3
Myrobalans 1	1.45	0.204	6.0	8.4	6.0	8.4
" 3	1.44	0.202	5.55	7.8	5.55	7.8
" (mean :—)	—	—	—	8.2	—	8.2
Mixed: Quebracho and myrobalans	0.80	0.112	3.1	4.3	3.1	4.3
Mixed: Quebracho and myrobalans	0.78	0.109	2.7	3.8	2.7	3.8
Chestnut	0.56	0.079	2.1	3.0	2.1	3.0
Hemlock	1.26	0.177	4.5	6.3	4.5	6.3
Cube gambier	3.2	0.450	7.7	10.8	7.7	10.8
Block gambier	3.1	0.435	11.6	16.4	11.6	16.4

It will be noticed that the nitrogen values of gambier are not only comparatively high, but also not very constant. This is doubtless due to the fact that gambier is an extract which contains a very variable amount of insoluble and unextracted matter; in short, gambier is an extract which is very badly manufactured. Nevertheless, the nitrogen value is even in this case of some value, for it is at any rate a check upon the addition of nitrogenous matters of animal origin, which are said sometimes to find their way into gambier.

It is quite possible that this determination of nitrogen values might yield another criterion for detecting the adulteration of extract with wood pulp. Not having any wood pulp extract to hand, the writer has been unable as yet to determine its nitrogen value, but its nature and origin make possible that its nitrogen content will be comparatively great. If wood pulp contains nitrogen in the same order of quantity as the dry tanning materials tested above, its presence in chestnut extract should be easily demonstrated by a determination of the nitrogen value of the suspected extract.

The nitrogen values of the dry materials may be calculated in the same way as for extracts, but do not possess quite the same value, being less constant for any particular material on account of their dependence upon two variables. Moreover, mixtures of dry

*From the Collegium, London, England.

materials are not often met with. In the case of sumac and lentisco, it is interesting to note that a nitrogen determination would be at any rate a confirmatory test for the adulteration of the former with the latter. In this case the tannin percentage is reduced whilst the nitrogen content is raised. Hence, if both these features are noticed, there is evidence of such admixture.

It is probable that the percentage of nitrogen leached out under tannery conditions will differ from that extracted in the manufacture of extracts, but some of this nitrogen is certainly leached out, and it is necessary to point out that in estimating nitrogen in tan liquors, the nitrogen originating in this way should be carefully distinguished from the nitrogen obtained from the goods.

All the nitrogens here recorded were by Kjeldahl's method. The digestion is slow, and it is not wise to employ permanganate as accelerator so long as the acid is turbid. When a clear red-brown is obtained, however, the digestion is soon completed if the useful suggestions of Mr. A. T. Hough¹ be adopted.

The directors of the Swedish State Railways have requested the submission of a bill in the present Riksdag for an appropriation of \$348,400 for the erection of a peat-powder factory at the Hästhagen bogs and for the use of enough locomotives for peat powder so that all the trains on the Falköping-Nässjö line may use this fuel. After a careful examination the railway directors state that they have found peat powder to be very efficient and practical for locomotives, with a fuel value, compared with that of coal, of about 2 to 3. The ratio of peat powder will probably be greater when it has been used and experimented with further. Therefore it is considered a good thing to use peat powder, especially as the country's own resources will be utilized. In order not to have to depend on private industry and the fluctuations of the market, the directors thought it would be advisable for the railways to have a peat-powder factory of their own, and estimates of the cost of erecting a factory have been given. The Hästhagen bogs have been chosen as a suitable place, as it is estimated that 20,000 tons of peat powder can be produced there annually for 20 years. This amount is required by the Falköping-Nässjö line for that period. Using the ratio given and calculating from the lowest estimate for its production, the cost of peat powder, per ton, would be 15 crowns (\$4.02) and the corresponding price of coal would be 22.50 crowns (\$6.03) per ton. When calculating the price at 15 crowns per ton the items included are: Cost of running the factory, interest on the cost of changing locomotives for the use of peat powder, patent cost, and royalty. The company that erects the factory will charge 25,000 crowns for the use of the patent and 50 ore (\$0.134) per ton of peat powder as royalty.

ADDITION AGENTS IN THE ELECTRO-DEPOSITION OF SILVER FROM SILVER NITRATE SOLUTIONS.*

By FRANK C. MATHERS and JOHN R. KUEBLER.

AIM AND RESULT OF THIS INVESTIGATION.

The aim of this research was to study the action of addition agents in restraining the characteristic, loosely adherent, crystalline structure of silver electro-deposited from silver nitrate solutions and, if possible, to discover a method of depositing solid, smooth and adherent silver cathodes.

The ordinary addition agents such as glue, peptone, clove oil, aloin, etc., were found to be either without appreciable effect or to prevent only partially the formation of crystals and in no case was a thick, smooth deposit obtained.

Tartaric acid was far superior to anything else that was tested. A bath containing three percent each of silver as nitrate, nitric acid and tartaric acid gave a smooth, hard and entirely adherent silver cathode.

By the simultaneous addition of 0.01 percent of glue every twelve hours, the amount of tartaric acid could be reduced to about 0.4 percent.

MANIPULATION.

Small beakers containing 100 cc. of the electrolyte were used as electrolyzing vessels. The electrolyte contained 3 percent of silver as silver nitrate and 3 percent of free nitric acid. Square pieces of pure sheet silver about 0.2 mm. in thickness and having a total area of 25 sq. cm. were used as cathodes. Anodes, also of pure silver, were melted in cupels with a blast lamp and a hole was made in each one by a small piece of wood which was thrust through the center of the molten silver. Two anodes, suspended by platinum wires, were suspended in each beaker. A current density of 0.8 amp. per sq. dec. (7.4 amp. per sq. ft.) was used. Each bath was continuously but gently stirred by a slow current of air bubbles from a glass tube which was drawn to a capillary at the end of the bottom of the bath.

ADDITION AGENTS OF THE USUAL CLASS.

Some of the addition agents such as clove oil, peptone and pyrogallol are oxidized by the free nitric acid with the formation of colored solutions whereby the action of the material is probably changed.

Glue, 0.02 to 0.04 percent, greatly lessened the crystalline structure. The projecting crystals upon the edges and at irregular places on the faces were fairly adherent. With increasing quantities of glue, vertical striations formed and finally with 0.26 percent, a spongy deposit was produced.

Peptone (0.04 percent was best) gave a striated, finely crystalline deposit of a white color but with projecting, crystalline edges. The deposit was bet-

¹Collegium, 1915, page 126.

*Paper presented at the 29th General Meeting of the American Electrochemical Society, Washington, D. C., April 27-29, 1916.

ter than the one with glue. An excess of either glue or peptone made the deposits spongy.

Gum Arabic slightly lessened the tendency to form crystals, but aloin and clove oil seemed to be practically without effect.

Pyrogallol and tannin, 0.05 percent, each produced a fluffy, voluminous, tinsel-like deposit which was easily shaken from the starting sheet.

The almost total failure to obtain smooth deposits with the above addition agents which are so successful with other metals, indicated the importance of trying unusual classes of addition substances.

INORGANIC ADDITIONS TO THE BATHS.

Orthophosphoric acid, 1 to 10 percent in baths containing 1 to 3 percent nitric acid, did not materially reduce the tendency to form crystalline deposits but in some cases the deposits seemed more adherent. Without free nitric acid, spongy deposits were obtained with the higher concentrations of the orthophosphoric acid.

Metaphosphoric acid, 1 to 2 percent and no free nitric acid, gave hard, firm, apparently non-crystalline, vertically striated deposits of a brownish color. Addition of nitric acid made the deposits slightly crystalline in appearance and of a white color. One percent of metaphosphoric acid and 3 percent of nitric acid seemed best. These baths gradually deteriorated, the deposits becoming more loosely crystalline. Except for this difficulty, this type of bath might be made satisfactory.

Boric acid produced no improvement.

The addition of 2 percent of the nitrates of ammonium, sodium, potassium, barium, strontium, calcium, or magnesium, or 10 percent of the nitrates of sodium, calcium or strontium produced no beneficial results.

ORGANIC ACIDS IN THE BATHS.

One percent of oxalic acid and 3 to 10 percent of nitric acid (the increased nitric acid was to redissolve the precipitate of silver oxalate) gave a spongy deposit. With 0.006 percent of oxalic acid and 3 percent of nitric acid no precipitate was formed in the bath but the deposit, which was finely crystalline and smooth in the beginning, gradually formed crystalline projections.

Succinic acid gave about the same results as the oxalic.

Lactic acid, 1 to 5 percent, and nitric acid, 1 to 3 percent, gave crystalline deposits. The higher the percentage of lactic acid, the smoother were the deposits. These deposits seemed as rough and coherent as those with the glue alone.

Picric acid, 0.5 percent, gave spongy deposits.

Tannic acid in small quantities gave loose, tinsel-like crystals. Larger amounts of tannic acid (0.5 percent) with 1 percent of nitric acid gave spongy deposits.

Citric acid, 3 percent, gave firm, dark, lustrous deposits which were free from any indications of loose

crystals. The effect was similar to that with tartaric acid except that the latter was more permanent and showed less tendency to make the deposits spongy.

Tartaric acid was the best addition agent found.

TARTARIC ACID AS AN ADDITION AGENT.

Concentration of the Baths.—Three percent of silver as nitrate was chosen because the commercial refining baths have about this concentration. The increase in the concentration of the silver to 6 percent very much improved the deposits, which became smoother especially on the edges. Increased cost would be the only objection to this higher concentration of silver.

The higher the percentage of nitric acid (0 to 1 percent), the more pronounced was the crystalline structure when low concentrations of tartaric acid (0.2 to 1 percent) were used. Continuous electrolysis of baths low in nitric acid (a few drops to 0.5 percent) finally produced poorly adhering deposits. This trouble could be avoided by adding more nitric acid at intervals. Three percent of nitric acid, the quantity used in most of these experiments, was chosen in order to avoid the necessity of making these repeated additions. If a lower concentration of nitric acid had been chosen and maintained, a lower percent of tartaric acid would have given as good deposits as the higher percent which was used in these experiments.

Deposits from baths with the tartaric acid varying from 0.1 to 8 percent were at first equally good as regards smoothness and firmness. The color varied from a light grey to a dark grey as the quantity of tartaric acid was increased. As electrolysis progressed this color gradually faded, becoming pure white in those baths containing the smaller amounts of tartaric acid and lighter grey or even merely slightly purplish in spots in those baths having the larger quantities of tartaric acid. The length of time the cathodes remained smooth and free from rough crystalline projections was directly proportional to the quantity of tartaric acid present. Three percent of tartaric acid was considered best; the greater smoothness produced by the larger quantities was not deemed sufficient to warrant the additional cost.

Use of crude cream of tartar.—Crude argols cannot be added directly to the baths on account of the large quantity of insoluble matter and the aqueous extract cannot be used because it contains substances which produce sponginess. However, the crude potassium bitartrate, obtained by crystallization of the aqueous extract from argols, gave as good deposits as refined tartaric acid except that they were a little rougher.

Effect of temperature.—Increase in temperature increased the formation of crystals. The deposit at 50° C. from a bath containing 3 percent tartaric acid, was as crystalline as the deposit from a bath with 0.5 percent tartaric acid at room temperature (23° C.). In the beginning a darker, smoother, more shin-

ing deposit was obtained at 13° C. than at room temperature, but the final cathode did not seem to be materially better.

Current density.—An increase in current density to 1.6 amp. per sq. dec. (14.8 amp. per sq. ft.) caused the cathode to become much rougher, some of the projections being easily broken off.

Firm, comparatively smooth deposits were obtained with higher currents from vigorously stirred solutions or from baths containing a higher percent of silver.

Use of impure anodes.—The use of anodes containing base metals, as lead, copper, zinc, etc., causes a decrease in the concentration of silver in the bath because the amount of silver deposited upon the cathode is equivalent to the total quantity of metals dissolved from the anode of which only a portion is silver. With a 3 percent silver solution and 900 fine anodes, between 5 and 6 ampere hours per 100 cc. of solution practically exhausts the silver in the electrolyte providing none of the base metals are deposited. To avoid this difficulty, silver nitrate must be added at intervals in sufficient quantity to maintain the desired concentration. Observing this precaution with a bath containing 6 percent silver as nitrate, and 900 fine anodes, a cathode weighing 175 grams was deposited from a 100 cc. bath. The cathode was exceptionally smooth and was free from irregular projecting places on the edges. At the end of the electrolysis, the bath contained 16 percent of base metals as calculated from the weight of anodes dissolved. In commercial refining, baths are discarded or purified when the impurities reach 4 percent in some systems or 8 percent in others.

Effect of inorganic substances in baths containing tartaric acid.—The deposits were made less firm and less solid by sodium or magnesium nitrate, more rough by copper nitrate, less rough by lead nitrate and were unchanged by zinc nitrate. These nitrates of the heavy metals showed such a small influence upon the deposits that other conditions might have been responsible for the small variations noted.

Ferric nitrate (2 percent) made the deposit very much smoother and darker in color. The smoothest cathode obtained in the work was from a bath containing 6 percent of silver, 3 percent of tartaric acid, 3 percent of nitric acid and 2 percent of ferric nitrate. The cathode looked and felt like a piece of polished, dark metal. Chromium and aluminum nitrates did not show this same action.

Sulphuric acid (0.5 percent) seemed to partly neutralize the effect of the tartaric acid. The deposit was as crystalline as if a much smaller quantity of tartaric acid had been used.

Metaphosphoric acid did not improve the deposits but it had an action as shown by the striations.

Organic addition agents in the baths containing tartrates.—Aloin and clove oil seemed without effect. B-naphthol made the deposit non-adherent.

Peptone (0.04 percent with 0.25 percent tartaric acid) gave a smooth, brownish colored, glistening deposit in the beginning, but the deposit gradually became less firm and finally became spongy.

The addition of 0.02 percent of glue twice daily caused the deposit to have a dark, shining, metallic appearance in the beginning but this metallic luster gradually changed to a mat surface. When 0.046 percent of glue had been added the deposit became partly spongy. This is the usual result when an excess of organic matter is present. The use of glue is recommended on account of the greater smoothness which it produces.

Good deposits were obtained by the addition of small amounts of glue to baths containing less than 3 percent of the tartaric acid. A firm but slightly rough deposit was obtained from a bath containing 0.25 percent of tartaric acid to which 0.01 percent of glue was added twice daily. After 56 grams of silver per 100 cc. of the bath had been deposited, some crystalline projections formed, an indication of the exhaustion of the tartaric acid. A firm, comparatively smooth deposit, weighing about 100 grams per 100 cc. of bath, was obtained from a bath containing 0.5 percent of tartaric acid to which 0.01 percent of glue was added twice daily. It was necessary to add more tartaric acid to this bath before another smooth deposit could be produced. The exhaustion of the tartaric acid was shown by the crystalline structure and the white color of the deposit which, however, was still tough and adherent.

A smoother deposit was obtained from the baths containing the glue and the smaller amounts of tartaric acid by using only 0.5 percent of nitric acid. More nitric acid should be added when the bath becomes dark colored.

Cost of the addition agents.—With tartaric acid at 30 cents per pound and glue at 20 cents per pound¹, the cost of these addition agents is 0.17 cent per pound (0.37 cent per kilo) of silver deposited. This assumes that 0.5 percent of tartaric acid and a total of 0.1 percent of glue are required and that only 100 gms. of silver are deposited from each 100 cc. of electrolyte. With 900 fine anodes, the bath would then contain over 8 percent base metal impurities and would have to be purified or discarded. The cost at present prices would be 0.23 cent per pound. These prices are for purified tartaric acid, whereas a crude cream of tartar gives satisfactory results.

Vigorous stirring of the baths.—A current of 2.4 amp. per sq. dec. (22.2 amp. per sq. ft.) was used in baths which were vigorously stirred with rotating glass stirrers. The edges of the cathodes became thick and projected somewhat, but this was almost prevented by increasing the concentration of the silver to 6 percent. However, smoother, more shiny deposits were obtained by using 0.08 percent of glue

¹List prices before the war.

(added in four portions) and 0.5 percent of tartaric acid. A somewhat smoother deposit was obtained by using greater quantities of tartaric acid.

Properties of the deposited silver.—a. Color. The dark, shiny color which was always noted in the beginning of each electrolysis gradually changed to white, except in the presence of ferric nitrate or repeated additions of glue in which cases the dark color persisted to the end.

b. Smoothness. In all cases the deposits became less smooths as electrolysis progressed. Ferric nitrate aided materially in maintaining the initial smoothness.

c. Hardness and structure. The deposits were hard but brittle. Cathodes only 0.5 cm. thick could not be broken by the hands but cracked into many pieces when struck with a hammer. Pieces from some of the cathodes showed distinct strata.

d. Occluded material and specific gravity. When heated, the cathodes swelled, becoming a fourth larger in some cases, and the deposited silver crumbled from the starting sheet, giving a great number of small, loose pieces of silver, if the temperature was kept below the melting point of silver. An odor of burning tartaric acid could be detected in some cases and if the deposit was dark, grey or shiny, the coloration disappeared and the mass assumed a silver white color.

The darker, smoother and more shiny the cathodes, the greater was the quantity of occluded material. Some analytical results are as follows:

Description of cathod.	Per cent loss on drying at 160° C.	Per cent loss from 160° C. to ignition with a Meker burner.
White, slightly crystalline.....	0.13	0.77
White, smooth	0.28	0.99
White. No swelling when heated.....	0.15	0.23
Shiny and smooth.....	0.64	1.22
Shiny and smooth.....	...	1.16

The loss at 160° C. seemed to be influenced by the length of time the samples had been air dried. All of the above samples were from baths containing tartaric acid but no glue.

The density of the air dried samples which were mechanically removed from the starting sheets varied from 9.84 for dark shiny samples to 10.07 for crystalline ones. After ignition until the sample had expanded to maximum volume and the color had become silver white, the apparent specific gravity of a shiny sample was as low as 8.8. The specific gravity was raised to 9.37 by putting the pycnometer under reduced pressure which caused a vigorous evolution of bubbles from the pieces of silver. This shows that the escape of the occluded substances during the heating puffed the silver into minute gas chambers. The specific gravities of different cathodes did not agree, due to the influence of the conditions of electrolysis which affected the quantity of occluded material and also to the effect of the temperature and time of heating and the size of the pieces of silver.

Current efficiency at the cathode.—A bath containing 3 percent of silver as nitrate, 3 percent of nitric

acid and 3 percent of tartaric acid gave a cathode efficiency of 101.8 as compared with a silver nitrate coulometer and 101.82 as compared with a copper coulometer. This shows 1.78 percent of impurities in each 100 grams of deposited silver, a number approximately equal to the loss on ignition for shiny silver given above.

REVIEW AND DISCUSSION.

About 10 percent of the silver output is electrolytically refined in solutions of silver nitrate containing nitric acid. For the most part, the silver is deposited in the well-known crystalline, non-adherent condition. There are many advantages in the deposition of the silver in a solid coherent form². Chemists at the United States Mint at Philadelphia devised the improvement of adding 0.008 to 0.01 percent of glue³ to the baths each day, whereby the cathode deposits were less crystalline and were coherent enough that vertical cathodes could be used and handled in the way ordinarily followed in electrolytic metal refineries. A c. d. of 8 amp. per sq. ft. (0.9 per sq. dec.) was used. The cathodes, as shown by a cut of a photograph⁴, were rough and crystalline and in no way comparable in smoothness with the cathodes obtained in this research by the use of tartaric acid. The use of glue which was adopted by other of the United States Mints⁴ has now been discontinued because it was of little value at the higher c. d. of 15 amp. per sq. ft. (1.6 amp. per sq. dec.), which was necessary for the sake of speed. It is said that the crystalline silver cathodes, without the use of any organic material, are coherent enough that they can be withdrawn from the baths if sufficient care is exercised.

This same action of glue in restraining the crystallization of the silver has been noted in silver nitrate solutions containing traces of nitric acid,⁵ in pure silver nitrate solutions containing no free nitric acid or other impurities,⁶ and in these same solutions using rotating cathodes⁷.

Tannin, pyrogallol and resorcinol are of no value and an excess makes the deposits non-adherent.⁸

Organic impurities of many kinds in pure neutral silver nitrate solutions were found⁹ to affect the character of the silver deposit which was "non-crystalline or imperfectly crystalline, depending upon the quantity of the impurity present." The things tried were: aqueous extract from various kinds of paper—filter, writing, blotting, rag and wood, pine wood shavings, silk, cotton and linen. The same effect was produced by glue, by Bredig's colloidal silver and by one percent additions of the following: hydrazine, hydroxylamine, dextrose, invert sugar, formaldehyde, acetaldehyde, furfuraldehyde, benzaldehyde; phenol, resor-

²Betts, Trans. Amer. Electrochem. Soc., 8, 121 (1905); Easterbrooks, *Ibid.*, 132.

³Annual Rep. of Director of U. S. Mints, 1905; Met. Chem. Eng., 4, 307.

⁴Eng. Min. Journ., 92, 301.

⁵Jarvis and Kern, School Mines Quart., 30, 100.

⁶Rosa, Vinel and McDaniel, Bull. Bur. Standards, 9, 209.

⁷Snowden, Trans. Amer. Electrochem. Soc., 7, 143.

cinol, hydroquinon, and phloroglucin. All of these substances which affect the silver deposit have the power of reducing solutions of silver nitrate to colloidal silver. Silver nitrite, silver hyponitrite, starch and cane sugar were without action on the silver deposit and they do not form any colloidal silver in the baths. The theory is advanced that the colloidal silver is the essential thing and that each particle of this colloidal silver which is deposited upon the cathode becomes a nucleus for a new silver crystal, hence the deposit becomes a mass of very small crystals rather than a much smaller number of large ones. Moreover, all deposits, where the addition agent has shown an action, are heavier than required by Faraday's Law. A weakness in this theory is that it cannot apply to solutions containing free nitric acid which would prevent the reduction to colloidal silver but the presence of the nitric acid does not prevent the action of the glue and other substances in restraining the crystallization of the silver deposit.

In the separation of silver from antimony, the silver has been deposited from solutions containing silver nitrate, nitric acid and tartaric acid in a non-weighable form and in a "faultlessly crystalline condition of silver luster."⁹ The action of the tartaric acid in restraining the crystallization of the silver was apparently overlooked, probably because the experiments were run, for the most part, in warm solutions, a condition which partly prevents the action of the tartaric acid.

Nitric acid or calcium nitrate in pure silver nitrate solutions increased the number of crystals in the silver deposit. Silver acetate increased the number of crystals 100 times, the deposit being like a "surface of frozen snow."¹⁰ Ammonium acetate was found to improve the deposits for quantitative work.¹⁰ These results show that the acetate radical is partly effective as an addition agent if we accept the idea that the function of an addition agent is to make the crystals very small and coherent but not so small nor so impure from absorbed addition agent that the deposit becomes spongy and non-adherent.

All of the organic acids tried in this work had an influence on the deposits which in most cases were made more finely crystalline and coherent. Only tartaric and citric acid gave smooth deposits showing little or no crystalline structure. These organic acids, tartaric, and to a lesser extent citric, acted very differently from the ordinary colloids. One important difference is the beneficial effect of large amounts of the tartaric acid while any excess of glue and other colloids or of some of the organic acids makes the deposit non-adherent. Tartaric and citric acid are not generally classed as reducing agents although the former does reduce silver from alkaline or even from neutral solutions. Any reducing action they might

have would be negligible in the presence of the free nitric acid. It seems that the effect of these acids cannot be due to their reducing properties.

Silver phosphate in phosphoric acid solution gave a spongy deposit.¹¹ Pyrophosphoric and nitric acid in silver solutions showed no advantage over cyanide for quantitative work.¹² No mention was found of the deposition of silver from solutions containing metaphosphoric acid.

No physical experiments were tried to determine the reasons for the beneficial action of the acids. Complexes between the silver, the tartaric acid and the iron, when present, might be the essential thing.

Addition agents in silver nitrate solutions only have been considered in this review and in this research.

SUMMARY.

Tartaric acid is the most effective substance for producing solid, firm deposits of silver from the ordinary silver refining bath containing silver nitrate and nitric acid. A good composition of the bath is 3 percent each of silver as silver nitrate, nitric acid and tartaric acid. The further addition of 0.01 percent of glue twice daily makes the deposit much smoother and of a darker, more shiny color.

The addition of 2 percent ferric nitrate to the above baths makes the deposits much smoother, darker and more shiny. Analysis of a cathode showed 0.086 percent of iron.

If economy in addition agents is desirable at the sacrifice of some smoothness in the deposit, 0.5 percent tartaric acid and 0.01 percent of glue twice daily can be used. More tartaric acid must be added after about 100 grams of silver have been deposited from each 100 cc. of solution, otherwise loosely adhering crystals are formed.

A current density of 22.4 amp. per sq. ft. (2.45 amp. per sq. dec.) in a vigorously stirred bath gave a firm, smooth deposit which was a little heavy on the edges. A current of 35 amp. per sq. ft. (3.8 per sq. dec.) gave a firm deposit with still rougher edges. In a bath only gently mixed or stirred, 7.4 amp. per sq. ft. (0.8 amp. per sq. dec.) gave the best results. With 6 percent silver solutions, 14.8 amp. per sq. ft. (1.6 per sq. dec.) could be employed.

The ordinary addition agents as glue and peptone, by themselves, only partly restrained the crystalline structure and did not produce smooth deposits.

Metaphosphoric acid caused the deposit to be hard and non-crystalline but the bath soon deteriorated.

The weight of tartaric acid used up is 0.005 of the weight of silver refined. The maximum cost of the tartaric acid and the glue at present prices is 0.23 cent per pound of refined silver.

The deposit is brittle, hence it is of no value in plating.

⁹Smith, Z. anorg. Chem., 3, 237; through Trans. Am. Electrochem. Soc., 26, 62.

¹⁰Fischer, Ber., 36, 3345 (1903).

¹¹Hughes and Withrow, Jour. Am. Chem. Soc., 32, 1573.

¹²Smith, Am. Chem. Jour., 12, 335.

¹³Brand, Z. anal. Chem., 25, 592.

SULPHURIC ACID PRODUCTION IN UNITED STATES IN 1915.

The production of sulphuric acid, expressed in terms of 50° acid, in the United States in 1915 was 3,868,152 short tons, valued at \$29,869,080 together with 189,795 short tons of oleum or fuming acid of different strengths, valued at \$2,787,971, making a total of 4,057,947 short tons, valued at \$32,657,051.

These figures, compiled by W. C. Phalen and just made public by the United States Geological Survey, include so-called by-product acid, or acid produced at copper and zinc smelters. The production of acid from this source in 1915 was 1,056,830 short tons, expressed in terms of 50° acid, valued at \$7,042,126, together with 59,189 short tons of oleum of different strengths, valued at \$579,115.

The production of acid is tabulated below:

PRODUCTION OF SULPHURIC ACID IN THE UNITED STATES IN 1915, BY GRADES, IN SHORT TONS.

Grade.	Quantity.	Value.	Price per ton.
50° Baume	1,518,271	\$19,681,246	\$ 7.04
60° Baume	657,076	4,976,453	7.57
66° Baume	1,019,024	14,211,381	13.95
Other strengths	189,795	2,787,971	14.69
Total	3,384,166	\$32,657,051	\$9.65
50°, 60° and 66° reduced to 50°	3,868,152	\$29,869,080	\$7.72

PRODUCTION OF SULPHURIC ACID FROM COPPER AND ZINC SMELTERS IN 1915, SHORT TONS.

Source.	Quantity.	Value.	Price per ton.
Copper smelters, 60°	360,522	\$2,749,633	\$7.63
Zinc smelters, 60°	484,942	4,292,493	8.85
Other strengths	59,189	579,115	9.78
Total	904,653	\$7,621,241	\$8.42
60° acid reduced to 50° Baume	1,056,830		

*Includes acid reported not only at 50°, but also at 52°, 53° and 55°.

†Includes stronger acid reported as oleum, etc., carrying varying percentages of free SO₂.

In the Geological Survey's preliminary statement on sulphuric acid, issued at the beginning of this year, the output of acid reduced to 50° Baume and that of stronger acids differ appreciably from that given above, though the totals differ only by a fraction of one per cent. This is due to a lack of differentiation in the returns received at the beginning of the year, whereby a considerable quantity of the stronger grades of acid were not reported as such but were included with 66° acid, were converted to 50°, and then reported in terms of this acid. The preliminary figures, therefore, for 50° acid are high, while those for oleum and the stronger grades are low, as compared with those tabulated in this bulletin, but the totals, as stated, differ only slightly.

During the last few years it has been customary to reduce different strengths of acid to 50° Baume whenever sufficient data were available for conversion, but as the production of stronger acid is becoming more important this will now be classed separately and no reduction will be made in terms of 50° acid. In the

preliminary statement, issued early in January, 1916, this separation was not possible.

Too much weight must not be attached to the values given in the tables, for sulphuric acid values have varied widely during the year. Producers who had previously entered into long-time contracts sold acid at prices much below those now current, especially during the last part of 1915. The trade in strong acids was active on account of the demand from the explosives and war munitions industries, but this demand came only after the first quarter of the year and was very strong only during the last half of the year. Before that time some acid plants were shut down. The average values given are therefore much below those which ruled on the market at the close of the year.

The above figures are final so far as the Survey's present information goes, but are subject to change, if necessary, when the printed report is issued. The changes, if any are made, will probably be slight.

MANUFACTURE OF REFINED SUGAR IN HAWAII.

According to the Daily Commerce Reports, 25 tons of refined white sugar are now being turned out daily by Kahuku Plantation at Kahuku, island of Oahu, 72 miles by rail from Honolulu. This is the second company in the islands to undertake the production of refined sugar, the first one to enter the field having been the Honolulu Sugar Plantation, whose plant is situated six miles from Honolulu. The experiment at the Kahuku Plantation was first undertaken six weeks ago, and while it was not publicly announced, as it was purely an experiment at the start, the fact that an attempt was being made to manufacture white sugar there by the "Dutch" process has been generally known. This process is a patented one. A vegetable charcoal impregnated with various colloidal chemicals, called "Norit," is added to the melted raw sugar, and complete clarification takes place after the juice is neutral. The white sugar now being turned out at Kahuku is not distinguishable from any other of the same class. While the process is a patented one, the fact that the vegetable char can be recovered and used over again, which is not true of the bone char used in the ordinary refining processes, is also a point in favor of the use of "Norit." The importance of the "Dutch" refinery method will appear at the end of this season's run, when the full 1,500 tons have been treated; but it will be some months before it can be determined whether the process will find general adoption in the Hawaiian mills.

Consul Harry G. Seltzer, at Breslau, Germany, reports under date of April 27 that one of the Breslau tinfoil factories has succeeded in providing a substitute for tinfoil by producing zincfoil. The new product is not to be distinguished from tinfoil and is supposed to render the same service.

THE REDUCTION TEST FOR TUNGSTEN.*

By M. L. HARTMANN,†

The recent activity and interest in tungsten has brought to our attention the methods for detecting this element. One frequently hears the remark that the qualitative tests are uncertain, and it was due to such a remark that this investigation of the sensitiveness of the reduction test for tungsten was begun.

Tungsten minerals when fused with an excess of sodium carbonate, give soluble sodium tungstate (Na_2WO_4). When solutions of sodium tungstate are made acid with hydrochloric or sulphuric acids, in the cold, a white flocculent precipitate is formed (composition varies from $\text{WO}(\text{OH})_4$ to $\text{WO}_2(\text{OH})_2$ which on heating becomes yellow tungstic acid or oxide (WO_3 or H_2WO_4). If a strong reducing agent is added, the solution is changed to a bright blue color, due to a suspension of a finely divided, flocculent precipitate, consisting of oxides of composition between WO_3 and WO_2 (sometimes given as $\text{W}_2\text{O}_5\text{W}_3\text{O}_8$, W_4O_{11}). If the reduction is carried still further, the brown tungsten dioxide (WO_2) is formed. This change was very slow at room temperatures, the blue precipitate having been kept for two days.

A rather extended investigation was made of the best method for making this qualitative test. For studying the reactions involved, a dilute standard solution of sodium tungstate was prepared. In brief the following results were obtained:

EFFECTS OF DIFFERENT REDUCING AGENTS.

The reducing agents usually recommended for this test are zinc and hydrochloric acid, tin and hydrochloric acid, and stannous chloride and hydrochloric acid. It was found that the use of tin and hydrochloric acid was the most satisfactory, as the evolution of hydrogen gas was not too violent, and the reduction was very rapid, due to the quadrivalence of tin. The use of zinc and hydrochloric acid was fairly satisfactory, but not as desirable as tin. The evolution of hydrogen was frequently so violent (in the concentrated acid solution required for the best results) that the blue color could not be detected in the solution. Furthermore, with very small amounts of tungsten the reduction was carried to the brown color so rapidly that the blue color escaped notice.

The use of stannous chloride in hydrochloric acid solution is not to be recommended for this test. The blue color was sometimes obtained when the concentration of the tungsten was high, when the amount of stannous chloride was large, and when the solution was heated for some time. Small quantities of tungsten could not be detected, using this reducing agent.

Hydrogen peroxide is sometimes used as a reducing agent in similar reactions. It was found that it did not reduce tungstic oxide either in the cold or when heated.

Oxalic acid is also used occasionally. This reducing agent was without effect on tungstic oxide.

THE EFFECT OF ACID CONCENTRATION.

Using zinc as the reducing agent, and hydrochloric acid at room temperature, and sodium tungstate solution equivalent to 0.01 grams of WO_3 in a total volume of 10 c.c., the blue color became distinct with 0.25 c.c. concentrated hydrochloric acid in one hour; with 0.50 c.c. concentrated hydrochloric acid, in two minutes; with 1.00 c.c. concentrated hydrochloric acid, practically instantaneously.

AMOUNTS OF TUNGSTIC OXIDE WHICH CAN BE DETECTED.

In a total volume of two cubic centimeters, with one-half cubic centimeter of concentrated hydrochloric acid, and with tin or zinc as the reducing agent, 0.0005 grams of WO_3 could easily be detected by the blue color. Using tin, the color was produced in the cold, while with zinc it was necessary to heat the solution to get an immediate color. If allowed to stand at room temperature, the blue color could be detected in half an hour.

Thus in solutions containing only tungsten salts the test is very sensitive. As small an amount as one milligram of WO_3 may easily be detected.

The above experiments were made upon pure sodium tungstate. In order to study the reduction test under actual conditions, ores of known tungstic oxide content were examined. Here, before the reduction test can be applied, the material must be brought into solution as a tungstate or in the form of tungstic oxide in finely divided or colloidal particles. There are two methods which can be used; fusion with sodium carbonate and subsequent solution, or solution of the ore in hydrochloric acid.

The following ores (Table I) were tested by both methods and the tabulated results obtained.

TABLE I.

		Reduction With Tin After Fusion, Solution in HCl.	
Material.	% WO_3 Solution in HCl.		
Wolframite			
Sand	3.0	No color	Strong blue color
Wolframite Ore	16.0	Strong blue color	Residue blue but not solution
Wolframite			
Concentrate ..	32.0	Strong blue color	Distinct blue color
Scheelite Ore....	38.0	Strong blue color	No color
Wolframite			
Concentrates	68.0	Blue residue and faint blue solution	Strong blue color
Scheelite	75.0	Strong blue color	Distinct blue solution and blue residue

From the tests made on these tungsten materials it was found not safe to depend upon a single method for all cases. Most of the ores dissolve sufficiently in boiling hydrochloric acid to give the blue color on reduction. The low grade ore did not respond to this treatment. In the method of fusion with sodium carbonate, it was found essential to have a large excess of sodium carbonate. This is to insure the complete transformation to soluble sodium tungstate. It was further found, that for the most accurate tests, the fused mass should be first dissolved in water and then

*From the Pahasapa Quarterly.

†Professor of Chemistry, South Dakota School of Mines.

made acid with hydrochloric acid. The reason for this procedure is to insure a colloidal precipitate of the tungstic oxide, which on reduction gives the blue solution, rather than the blue residue which forms when the fusion is dissolved in hydrochloric acid.

In conclusion, the following general directions can be recommended for testing for tungstic oxide in ores. Boil at least 0.2 grams of finely divided material in a small test tube with concentrated hydrochloric acid until about one-half the acid is evaporated. Dilute with an equal volume of water, add a piece of metallic tin (mossy) and heat if necessary. A fine blue color indicates the presence of tungsten. If this test gives negative results, about 0.5 gram of the material should be fused in at least 4 grams of sodium carbonate. (This may be done with an ordinary Bunsen burner in a metal crucible, or before the blast in a porcelain crucible.) Dissolve the fused mass by boiling water in the crucible. Acidify the aqueous solution with an equal volume of concentrated hydrochloric acid, add a piece of metallic tin, and warm if necessary. The volume of the solution should not be more than 10-20 c.c. A fine blue color indicates the presence of tungsten. In either case, if reduction is continued long enough, a brown color is obtained.

These tests if properly used, will show the presence of tungstic oxide in materials as low as two per cent, and by using special precautions, will detect tungsten in even lower grade materials.

NOTE.—The interfering colors which might be produced by other elements present, under the conditions of the test for tungsten, are being studied at the present time. Columbium (Niobium) gives a blue color which is said to disappear on dilution and which does not become brown after long reduction. Vanadium also gives a blue color on reduction, but tartaric acid will cause this reduction, whereas it will not reduce tungstic oxide. Molybdenum on reduction goes through a series of color changes from violet to blue to black. Titanium gives a violet color. No other elements are likely to interfere with the test for tungsten.

The U. S. Civil Service Commission, Washington, D. C., announces an open competitive examination for assistant alloy chemist, for men only, on July 5 and 6, 1916, at the places mentioned in the list printed hereon. From the register of eligibles resulting from this examination certification will be made to fill a vacancy in this position at a salary of \$1,620 per annum in the Bureau of Mines, Department of the Interior, for duty at Ithaca, N. Y. The duties of this position will consist of assisting in an investigation covering the methods of preparing nonferrous alloys, the furnaces and other appliances used in their manufacture, and the prevention of waste in their production. Applicants should have a knowledge of physical chemistry, with special reference to the phase rule and its application to commercial and scientific problems; and a reading knowledge of French and German. As an insufficient number of applications were received for the examination for this position announced to be held on May 17 and 18, 1916, qualified persons are urged to enter this examination.

LIQUID CHLORINE.*

By G. ORNSTEIN.

You are all familiar with the element chlorine, its history, manufacture and characteristics, so that it will be hardly necessary to go into great detail on this subject.

The first process employed commercially was the same which we have all used as students in the laboratory—namely; that of generating it from manganese oxide and acid, which may be either muriatic or a mixture of salt and sulphuric acid. This process later on was made eminently practical by Weldon's invention of recovering the manganese oxide by means of addition of lime to the waste liquor, blowing air through the mixture and returning it in this regenerated form to the process. This Weldon process is the only purely chemical process, operated on a commercial scale, which furnishes a chlorine gas of sufficient concentration to be used for liquefaction. The Deacon process, in which hydrochloric acid fumes are decomposed in the presence of air and a contact substance, such as copper chloride, gives a diluted gas, and therefore is not practicable for the purpose of liquefaction, at least not directly.

To overcome this drawback, in this and other instances where a weak chlorine gas is obtained, several processes protected by patents have been worked out, particularly by Goldschmidt and Sperry, which aim at absorbing the chlorine from a weak mixture, the former by stannic chloride, the latter in the form of chlorine hydrate, thus separating it from the diluting impurities, and later on decomposing it again by application of heat, for the purpose of producing pure chlorine. In the Acker process, in which an extremely poor gas was obtained, one even went so far as to first convert the chlorine into bleaching powder and to subsequently decompose it by acid.

However, it seems that none of the chemical processes are operated at present for the purpose of liquefaction, except perhaps in a few individual instances and the chlorine liquefied nowadays, here as well as abroad, is almost entirely produced by electrolytic processes.

The electrolytic decomposition of brine, or potassium chloride, is known to you in principle. It consists in passing an electric current of high amperage through an electrolytic cell, in which the anode is made of carbon, or, what is much to be preferred, Acheson graphite, or fused iron oxide, and the cathode of iron, either in the form of a perforated sheet, wire screen, or in some instances a solid sheet, depending on the details of construction.

When the electric current is passed through the cell,

*Paper presented at a joint meeting of the New York Sections of the American Electrochemical Society, American Chemical Society, and Society of Chemical Industry, Feb. 11, 1916, and called up for discussion at 29th Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

the brine is split up into its components, chlorine which escapes at the anode, and caustic soda or caustic potash at the cathode. The products of the electrolysis have to be kept apart, as otherwise they will combine again forming hypochlorite and eventually chlorates, and quite a number of different forms of apparatus have been made and patented to prevent this re-combination. In the majority of cases, diaphragms of various designs are employed (for instance, in the Gibbs, Townsend, McDonald and Bilter cells) the basis of which is mostly asbestos. In others they are kept apart by gravity and by causing a constant flow of liquid in the direction from the anode to the cathode. This principle is employed in the Bell process and others.

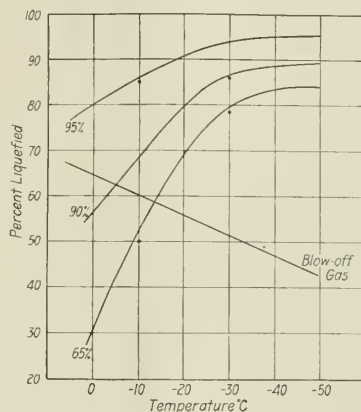
A third principle is employed in the mercury cell, in which the cathode is mercury instead of iron, absorbing the sodium or potassium under the influence of the electric current, and this in return is released again by water, outside of the electrolytic cell, in the form of caustic. The pure mercury is then again returned to the cell and reloaded at the cathode, but no matter what the construction of the cell may be, in all instances a highly concentrated chlorine can be obtained which, with graphite or iron oxide anodes, which are less subject to electrolytic oxidation than carbon, should easily yield gas of 97 to 98 per cent purity, the balance being carbon dioxide, electrolytic oxygen and a slight trace of air. With iron oxide electrodes no carbon dioxide can be formed, but the amount of electrolytic oxygen will be correspondingly higher. However, only in a few cells is a gas of this purity actually obtained, on account of mechanical defects, such as leaks in the cell covers, or pipe lines, or through negligence of the cell attendants.

For the liquefaction of chlorine it is of great importance that attention should be paid to generating highly concentrated gas, because otherwise the percentage which can be liquefied from a certain volume of chlorine will decrease rapidly with each per cent of impurities. The following curves illustrate the influence of concentration as well as of pressure and temperature. For the figures on which these curves are based I am indebted to our works manager, Mr. Neuhaus.

The unliquefied residue, which still contains between 55 and 65 per cent of chlorine, is called blow-off gas and is released from the liquefying machinery, from time to time, when the pressure exceeds certain limits. It is generally conveyed to the bleach chambers, which is the preferred way of both using and getting rid of it, as on account of its dilution it can be used only for a limited number of other purposes. In any case, absorption capacity of some kind has to be provided, and it therefore appears that a chlorine liquefaction plant can be operated to advantage only in connection with the manufacture of other chlorine products.

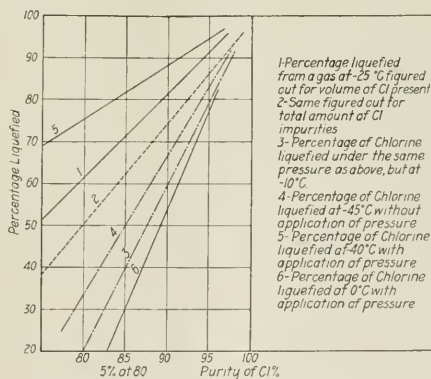
There have been a great many attempts to liquefy

chlorine, ever since the beginning of the nineteenth century, but until recently they were largely confined to laboratory experiments of no practical value. The first liquid chlorine was obtained in 1805 by Northmore, and as early as 1823 Faraday demonstrated the



Influence of Temperature on Liquefaction.

well known experiment which you find in every text book—namely, the decomposition of chlorine hydrate in a sealed and bent glass tube in which the hydrate is heated in one branch of the tube and the escaping chlorine liquefied in the other one, which is cooled



Influence of Pressure on Liquefaction.

down in a freezing mixture. But until after 1880 nothing was done towards working out a commercial process.

Between 1880 and 1890 a number of processes were worked out which at least made an attempt to produce liquid chlorine on a commercial scale. For instance, Vautin attempted to compress chlorine gas by pumping air into tanks containing chlorine and at the same time cooling it down to a low temperature. Others, Hannay and Marx, for instance, based their

processes on the decomposition of chlorine hydrate in a closed vessel. Heizerling first compressed chlorine, cooling it to a low temperature, and then liquefied it by sudden expansion. None of these were successful, and commercial liquid chlorine remained an unrealized dream until the arrival of the process of Knietzsch, of the Badische Co., who in 1888 placed the first liquid chlorine on the market. He was the first to realize as being of fundamental importance that for commercial liquefaction a chlorine had to be used which was both highly concentrated and free from moisture, two points which the above-mentioned inventors had overlooked. He also found that chlorine carefully dried did not attack iron or a number of other metals employed for building commercial machinery, and through an ingenious device of a so-called liquid piston, which is illustrated on the accompanying figure, he was able to put the chlorine under a high pressure without any danger of leaks through the stuffing box around the piston, causing corrosion, etc. The liquid media which he applied consisted of a column of petroleum around the piston and under this and in the other branch of the U-shaped cylinder he used concentrated sulphuric acid. The liquid piston was lifted up and down by a plunger moving in the petroleum and thus sucked in and compressed chlorine gas, which through a separator was carried on to a condenser where under the influence of low temperature it liquefied and was then filled into the shipping containers. He also heated the sulphuric acid by a steam or hot-water jacket, in order to reduce the absorptive power of the acid for chlorine gas.

According to my knowledge, most processes which are now in operation are still based on this fundamental principle; namely, all of them are using a liquid for compression; and while they may have been simplified in some way, for instance by omitting the petroleum and not heating the sulphuric acid, or by making changes in other directions, compressing the chlorine by entrainment, or in two or three-stage compression, yet in almost every case the principle has been maintained.

There are several processes on the market, for instance that of the Linde Co. of Germany, by which liquefaction is effected simply by cooling to -45° C. or lower, without any pressure, but the drawback of this process is that the percentage liquefied is lower throughout than that obtained with the combined system of compressing and cooling, as has been illustrated by the curves shown previously.

Regarding the relative merits of the various processes must hesitate to express an opinion. There is so much secrecy observed in this field, as in all lines of chemical industry, that I do not know enough about the details of construction and operation used by most of the other manufacturers to warrant my passing comparative criticism on this subject.

In one point I feel that "the people who know" will

agree with me; stick to what you have got and tried out in the course of years and of which you have studied all the little knacks and moods, and never mind what excellent results the other fellow "says" he gets. I would rather hunt for trouble in a 12-cylinder automobile motor than tackle a chlorine compressor when it is in the mood of the "morning after the night before."

The chlorine is shipped in steel cylinders, containing about 100 lbs. (45 kg.) net, weighing empty 70 to 100 lbs. (32 to 45 kg.). For large quantities it is also shipped in tank cars. The pressure in these containers varies with the temperature, but will drop rapidly on account of the heat absorbed by the evaporation if chlorine is drawn off continuously, even in relatively small quantities. In one place where chlorine was drawn off continuously for the purpose of water sterilization at a room temperature of about 2° C. the pressure dropped in 24 hours from around 55 to 15 lbs. per sq. in. (3.7 to 1 kg. sq. cm.), although not more than $\frac{3}{4}$ lb. (0.35 kg.) per hour was taken from a set of 4 cylinders. This cooling or freezing action can be easily counteracted by playing steam on the cylinder until the frost which will form has disappeared, placing it in a tub with warm water, or in a cabinet which is kept warm by artificial heat, or other similar means.

Liquid chlorine was unknown in the United States until the year 1909. Prior to this date quantities of liquid chlorine had been imported from Germany, but these were used solely for experimental purposes on a more or less extensive scale, but the United States did not begin any manufacture until the year above mentioned. It was in the beginning of this year that the Electro-Bleaching Gas Company, after about two years of experimenting, erected its first compressors, and a short while later two more chlorine concerns started in operation: the Goldschmidt Detinning Company and the Castner Electrolytic Alkali Co. The Goldschmidt Company used the product largely for their own purposes, namely, the detinning of tin scrap, whereas the Electro-Bleaching Gas Company had to find and build up a market for this entirely new product.

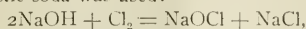
The two most important fields to which the liquid chlorine was to be introduced were the bleaching of vegetable fibre, such as cotton, flax, and paper pulp, and chlorination of all kinds, such as of ores, organic compounds, pharmaceutical products, etc. Most of all, it was necessary to instruct our purchasers how to use it for their various purposes, and we still recall with considerable pleasure the many comical occurrences which happened at that time. In one textile mill they apparently thought the cylinder contained something like a liquid bleaching powder, which they had been accustomed to use for generations. So they simply attached a hose to the valve outlet and tried to empty the cylinder into a vat containing water for diluting to proper strength. The result can be easily

imagined. After a minute or two there was nobody left in the mill who could be induced to enter the place and shut off the valve, and the letter we received was anything but complimentary; many other episodes of a similar nature occurred.

Therefore, before we could market the product we had to instruct our purchasers how to use it, and we were compelled to make demonstrations of how to prepare the bleach liquor and how to bleach yarn with it, in one mill after the other, until finally we succeeded in convincing a number of the largest and most conservative mills of the decided advantages of liquid chlorine as compared with bleaching powder; for the past four or five years they have definitely abandoned the latter in favor of the former.

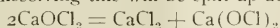
At the beginning we had to convince many chemists that the amount of available chlorine present in a bleaching solution prepared with liquid chlorine and alkali, such as soda ash, was equal to the full amount of chlorine passed in. They based their objections on the equation:

$\text{Na}_2\text{CO}_3 + \text{Cl}_2 + \text{H}_2\text{O} = \text{NaCl} + \text{HOCl} + \text{NaHCO}_3$,
or if caustic soda was used:

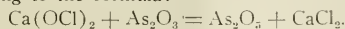


and insisted that these proved that one-half of the chlorine was converted into NaCl and thus wasted for bleaching purposes.

The assumption was that in bleaching powder the available chlorine was present in the form of CaOCl_2 , which as a matter of fact is the usually accepted formula for the powder, thus giving the impression that all the chlorine present was in the available form. But upon dissolving this will be split up according to:



so that one-half of the chlorine is converted into available chlorine and the titration with As_2O_3 proceeds according to the formula:



Thus it can be seen that the so-called "available chlorine" does not represent the actual amount of chlorine present in the hypochlorite but only half of it, and is rather an expression for the available oxygen in the same compound, which, if expressed in chlorine value must, on account of the bivalency of the oxygen and the monovalency of the chlorine, naturally be twice as high.

It follows now, by comparing the above equations, that the chemical reactions of both bleaching powder solutions and those made with liquid chlorine and alkali are identical and the fact can be no longer astonishing that by using liquid chlorine for the manufacture of bleaching solution an available chlorine content is obtained substantially equal to the number of pounds of chlorine absorbed by the solution.

We were able to show, and in connection with this wish to acknowledge the valuable assistance rendered us by Dr. J. M. Matthéys, that bleach solution thus prepared gave decidedly better results than bleaching powder. We could demonstrate that only one-half

of the amount of available chlorine, and even less, is required to be present in order to give the full bleaching results which formerly had been obtained with chloride of lime, and the tensile strength of the goods was correspondingly improved.

A large reduction of the so-called "sour," that is, the use of weak sulphuric or muatic acid after the bleaching bath for destroying the last traces of residual chlorine, also served to improve the strength. The explanation for its increased efficiency seems to be that in case a bleach is used in which the chlorine has been combined with soda ash, the presence of free hypochlorous acid causes a more rapid and more efficient action on the fibre than the neutral calcium hypochlorite. In addition, any bleach prepared with soda as a basis and with entire absence of lime salts seems to have a higher penetrating power on the cloth on account of no substances being present which are capable of forming insoluble precipitates on the fibre, a theory which is substantiated by the observation that a hard twisted yarn or cloth requires less available chlorine, as compared with the necessary quantity of bleaching powder solution, than a material of a looser texture.

Another large field in which liquid chlorine is now used extensively is for clinical chlorination processes, in which the quantities consumed are not large enough for warranting a concern to build a branch factory near the chlorine-producing plant for receiving the gas directly from the cells, and in which instance, therefore, liquid chlorine, being easily transportable, is the only other choice.

A number of manufacturers have tried to make the chlorine themselves from either bleaching powder and acid or manganese oxide and acid, but in most instances they have found that it was much more to their advantage to purchase liquid chlorine ready made; because in addition to the cost of the raw materials, which in either case exceed that for which liquid chlorine can be purchased, the latter has the advantages of being absolutely dry, chemically pure and under a pressure so high that it may be easily conveyed to any point of application and forced through liquids to be treated without the troublesome medium of blowers, fans, pumps, etc.

The valve of the chlorine cylinder, also, permits of an easy and accurate regulation, whereas the above mentioned chemical processes after being once started cannot be regulated at will unless a gas meter is used in connection with them, which only introduces another source of trouble, because as the only sealing medium concentrated sulphuric acid must be employed.

Of the advantages just cited, its purity is one of the most conspicuous characteristics of liquid chlorine. When a fresh cylinder is opened it will usually yield at once a gas which is 96 to 98 per cent pure, and after several pounds, from 3 to 5, have been taken

out it goes up to 99 per cent and after another pound or two it will be at 99.7 and 99.98 per cent, and will stay there until the last drop of liquid has evaporated from the cylinder. With these figures, which can be easily substantiated at any time, liquid chlorine may justly be called one of the purest, if not *the* purest, chemical on the market. The initial slight amounts of impurities represent the small traces of air, etc., which were in the gas coming from the cells.

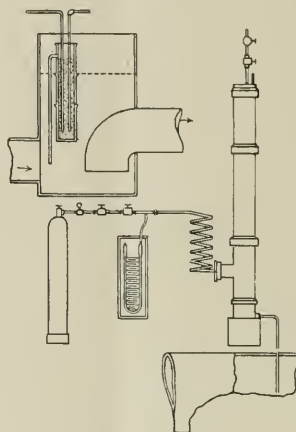
A third large field for the use of liquid chlorine has been opened up during the last three years, namely, its use for the sterilization of city water supplies and sewage. In this field as well as in the bleaching industry liquid chlorine had to fight again its old competitors, bleaching powder, and we are proud to say it made a pretty good showing even without making allowance for its youth and lack of experience.

After some experimental work had been done, the first commercial machines were installed in the Western New York Water Co. plant at Niagara Falls, N. Y., in November, 1912, where we received valuable assistance from Mr. F. H. Huy, general manager of the plants, and in Wilmington, Del., in January, 1913, where they are still in continuous satisfactory operation. They are based on the principle of absorbing a measured quantity of chlorine in a small amount of water, and subsequently adding this solution to the water to be treated. This so-called absorption process has the advantage of an even and rapid distribution of the sterilizing agent throughout the whole body of water, an advantage which is particularly apparent in large installations such as the Torresdale filter plant in Philadelphia, in which from 220 to 330 million gallons (1 to 1.5 million cubic meters) of water is filtered daily.

It is, furthermore, of advantage in plants in which the water to be treated is under high pressure, which in some places exceeds the pressure of the liquid chlorine itself. In these installations the application of the chlorine in the form of a solution which is forced into the main by means of a specially constructed pump is the only form in which the problem can be solved.

In the field of water sterilization the Leavitt-Jackson Engineering Co.'s apparatus is deserving of particular mention on account of the original principle involved, which consists in feeding the chlorine into the water by weight, by a balanced beam construction acting on the chlorine feed valve, an excellent construction mechanically but not sensitive enough for the minute quantities of chlorine which are required by the large majority of water works. The principle used in our first machine comprises the pressure regulation by a reducing valve or by two switched in series, the measuring of the rate of flow by the pressure difference caused by it on both sides of a calibrated orifice, and a subsequent absorption of this measured quantity in water prior to its addition to the main flow of water.

Under the conditions shown in the figure, where the chlorine in the absorption tower is discharged against atmospheric pressure, it is unnecessary to connect the U-tube to the down-stream side of the orifice, as would have to be done were the chlorine to be discharged against pressures higher than atmospheric. We are also using a "rate of flow" meter for measuring the chlorine. Through constructions along these lines it has been possible to effect an accurate regulation of chlorine gas to any quantity as small as 1/40 ounce (0.7 g.) per hour and as high as 25 lbs. (11 kg.) per hour, irrespective of any variations of the pressure in the cylinder, which in the course of operation



Ornstein Apparatus for Sterilizing Water.

may drop from 100 to 15 lbs. (7 to 1 atmospheres) without influencing the rate of feed.

To thoroughly realize the importance of employing a sterilizing agent which can be added under perfect control as to its quantity, it is sufficient to point out the necessity of adding it to a continuously flowing stream of water, and that it has to be mixed and intermingled with it continuously, thoroughly and evenly. This is not possible with chloride of lime, because the devices used for this purpose, such as orifice boxes, etc., will after a short time be partly or entirely plugged up by a lime deposit and be in full working order only for a few days at a time. We have also succeeded in developing apparatus capable of automatically varying the amount of chlorine added in proportion to the rate of water flowing.

Further advantages which may be cited in favor of liquid chlorine are: absence of taste and odor in limits very much wider than those prevailing for bleaching powder, no sludge or dust, smell or other nuisance, and particularly its *efficiency*, which is 2 to 3½ times as high as the same amount of available chlorine present in bleaching powder, or in other words, one pound of liquid chlorine has approximately the efficiency of 6 to 10 lbs. of chloride of lime.

In these various directions we had first to overcome considerable prejudice on the part of the communities, particularly as regards taste and odor. To what extent prejudice may sometimes run away with the common sense of the people may best be learned from the fact that complaints about chlorine taste and odor came pouring into the office of the Board of Health in Buffalo for four weeks *before* our machines were installed.

The results obtained by this process and applied by these machines have been highly satisfactory, as can be gathered from the Board of Health records of the various communities. Cities which formerly had an exceedingly bad record for typhoid fever are now reported as being almost or entirely free from it, and in no case whenever typhoid fever occurred in a community has it been possible to trace these back to the water used, but the reasons were always found in causes other than the city water supplies, such as milk, impure food, etc.

The war has naturally had considerable influence on the liquid chlorine trade, though the causes are entirely different from those which are responsible for the demoralization of prices of other chemicals. For the latter, the present situation is caused simply by the fact that these chemicals were hitherto imported from abroad and only small quantities, if any, manufactured here. Now the supplies being entirely shut off, prices, of course, have gone sky-high. Liquid chlorine, on the other hand, is an entirely domestic material which, therefore, could not be influenced by the shutting off of imports as to the quantity available. The increase in the trade and the price of liquid chlorine must principally be traced back to the shortage of bleaching powder, of which formerly more than 50 per cent was imported, and on account of its being shut off its price has risen from about \$23 per ton to figures between \$200 and \$300, whereas the price of liquid chlorine has only increased from \$160 to \$200 per ton to \$240-\$300. Taken in figures of available chlorine, which is the standard by which, apart from other considerations, the comparative values of the two materials are measured, this is now worth in bleach containing 35 per cent available chlorine \$570-\$860 per ton.

How long these conditions will continue to prevail is hard to say. Several of the big manufacturers are enlarging their plants and their bleach capacity, which may to some extent relieve the present shortage, but scarcely enough to reduce prices to anywhere near normal. The enlargement of plants, however alluring, is carried out very conservatively, realizing that after re-establishment of peace imports will begin again from Europe, particularly from Germany and England, perhaps not immediately, as some assume, but soon after. In the meantime the price of liquid chlorine may still travel a long way upward before approaching the present value of available chlorine in bleaching powder. Owing to this condition, manufac-

turers have been much tempted to divert part of the chlorine from the liquefying machinery into the bleach chambers, and a certain stringency may have been caused by this as well as by the exportation of moderate quantities for war purposes.

From the reports we have received from the other side of the Atlantic, liquid chlorine as such has been used as a weapon for incapacitating the enemy. To what extent these reports are strictly true and what part liquid chlorine as such has played in it, we do not know. I have read only one report, in one of the medical journals, which seems to be entirely unbiased and therefore in fair accordance with the facts, free from newspaper sensationalism and similar causes for one-sided treatment of the case. The report mentions more or less severe affections of the breathing organs, so severe in some instances that it seems incredible, according to my experience, that they should have been caused by inhaling of chlorine gas. Of course, I do not doubt that chlorine can be very detrimental to the human system in a closed room, from which there is no escape, but in the open air with a wind blowing, no matter how gently, it seems next to impossible that any suffering beyond that of temporary coughing spells, vomiting, etc., could possibly be caused.

It has been suggested from various sides, and it is undoubtedly a fact, that the chlorine, if employed, is mixed with other ingredients, such as bromine, sulphur and others, which would cause more severe and more lasting irritations than chlorine alone. I know personally of one instance in which sulphur has been used in connection with liquid chlorine.

We naturally have had a long experience in this line, particularly at the start when we had to struggle with a good many imperfections, leaks, etc., and never in any instance have we seen any lasting detriment suffered by any of our men. I have also had several years' experience in Germany along the very same lines, and there also have never been able to observe one single case of this kind. To appreciate this statement fully you ought to see into what kinds of atmosphere our men had to go sometimes without using any protection whatsoever, and when they had swallowed half of our production and were coughing violently they took a drink of Rexall's A. B. C. seltzer or bromo-seltzer, and a few minutes later were back in the plant. These compounds, as well as any other of a stimulating or nerve-relaxing influence, seem to be the best antidote for chlorine, among them a good stiff drink of whisky. If these are not available, inhaling of alcohol, chloroform or tetrachloride of carbon vapors spread out on a handkerchief will give speedy relief, but with the two latter ones one should be careful that no narcotic effect takes place. The inhaling of ammonia, which is recommended in several text-books, should be absolutely rejected, because in most instances the irritation grows only worse instead of better.

Prevention is better than cure, and the best prevention of inhaling too much chlorine is not to be afraid of it and if a whiff of it gets into the nose not to stop breathing abruptly. If you do, and if you cannot get out of the room before you have to breathe again, you are bound to take a deep breath which will carry the chlorine to all the tender parts of your lungs and a violent cough spell will be the result. If on the other hand, you continue to breath lightly, without taking a deep breath, you can stand a pretty strong chlorine atmosphere for minutes at a time, without any muzzle, safety helmet or other protection. Be careful, however, not to inhale the white fumes which are formed by ammonia and chlorine, in the course of trying to locate chlorine leaks with a rag soaked with ammonia. The coughing spells and the effect on the eyes caused by them are very much worse than with chlorine alone, and last longer. Also wet chlorine such as emanates from a saturated chlorine water seems to have worse effects than the dry, although only slightly more so.

We have in our plant an oxygen safety helmet, but except for purposes of keeping our men trained in its operation I have never seen it in actual use.

Another purpose for which undoubtedly quantities of liquid chlorine have been shipped abroad from this country is for the manufacture of picric acid, which, in this instance, can be made by first producing chlorobenzol, nitrating it, and then replacing the chlorine by hydroxyl, by treatment with alkali. These are the two only purposes for which, as far as I know, liquid chlorine has been used for war purposes. However, as you see, they are rather limited in their effects and, therefore, hardly deserving of the prominent place accorded them in the newspapers.

In general, I may say and I hope I have been able to demonstrate it in this paper, that liquid chlorine is much more important for peaceful than for war purposes, and we are taking considerable pride in the fact that in the past few years we have been able, instead of causing destruction of human lives, to save them from the ravages of typhoid fever, and in this way to prove that instead of being an enemy, liquid chlorine is becoming more and more a help and a boon to mankind.

In 1915 the zinc properties in St. Lawrence County, N. Y., were actively developed, and a 200-ton mill was in successful operation during the later part of the year. The Northern Ore Co. was the only producer of zinc in the state in 1915, though it is probable that at least one other company will operate in 1916.

The copper produced in Pennsylvania is a by-product separated from magnetic ores of the Cornwall iron mine, in Lebanon County. A small production of lead in 1915 was reported from Mercer County, but no production of gold, silver, or zinc has been reported.

VARNISH ANALYSIS AND VARNISH CONTROL. I—MOLECULAR WEIGHTS OF VEGETABLE OILS.*

By MAX Y. SEATON and G. B. SAWYER.

Modern methods of analysis and control have only recently been applied to the products of the varnish-making industry. Physical chemistry has, in particular, been the last branch of the science to find application in this field. Although physical constants of varnishes have been determined as a matter of routine testing for a great many years, investigation has in general stopped with the determination of such constants as viscosity or gravity and the relation which variations of these constants bear to variations in the treatment in the varnish kettle has but recently been appreciated.

Considerable work in the determination of physical constants of varnishes and the causes for the variations in these constants has been done in this laboratory, together with much work on the chemical properties of the products produced. It is planned to issue a series of papers covering as much of this work as is available for publication. The first paper, which follows, will deal with the determination of molecular weights of the vegetable oils used in the varnish-making industry and will indicate the molecular weights of some of the resulting products.

The literature pertaining to the composition and reactions of the oils commonly used abounds in references to the molecular weights of both the raw and the heat-treated oils. The inter-molecular changes which occur during treatment of the oil in varnish-making processes are admittedly very complex. Determination of molecular weights has recently been found valuable for their study and has been widely used by various authors.

In the attempt to apply the usual methods for the determination of molecular weights of substances in solution to oils and varnishes, so many difficulties have arisen that it has been necessary to investigate the use of a number of solvents, until finally one was found in which consistent molecular weights could be obtained. This paper, then, will cover the investigation of methods for the determination of molecular weights of oil and varnish products, together with a description of a suitable and accurate method.

The observed molecular weight of a vegetable oil or of a varnish mixture is in every case merely a mean or average molecular weight of the several substances which may be present. Thus, the most simple substance which will generally be investigated, linseed oil, will contain the glycerides of a number of different fatty acids together with small amounts of alcohols and traces of other substances. Under no circumstances can the molecular weight be looked at as being as definite a constant as it is in case of a pure material, but it can, nevertheless, give much information as to the composition and properties of the material investigated.

*From The Journal of Industrial and Engineering Chemistry.

The literature in which most complete record of molecular weight determination in this field appears refers to the mechanism of the polymerization reactions both of linseed and China wood oils. In this connection Maquenne,¹ Lewkowitsch,² Genthe,³ Morrell,⁴ Normann,⁵ and others, have reported determinations using the boiling point method in ether and in benzol, and the freezing point method in benzol and glacial acetic acid.

In general, results of previous investigators show a comparatively wide variation in the values obtained. Some difference is naturally to be expected on account of the different sources and accordingly different composition of the oils studied, but the values reported differ too widely for the difficulty to be ascribed to this source. There is a dearth of information as to the exact details of the methods used, so that in most cases critical examination is impossible. Of extreme interest, however, is the observation of Normann,⁵ who shows that varying values are obtained in different concentrations of solution. Normann obtained these results in an investigation of the molecular weight of raw and polymerized oils and although he details in full the results of his experiments he does not suggest a remedy for the trouble indicated. As far as the literature available to the writers indicates, his observation is the only one of this type which has been reported on such molecular weight work.

In a number of cases various authors have reported molecular weights of the acids prepared by saponification of the oils. It is probable that such a device has been used, owing to the greater solubility of the acids in most solvents, and also to the fact that by the use of the acids, solvents of the type of glacial acetic acid are made available. Such solvents cannot be used on the original oils on account of low solubility. In many instances where the molecular weights of the acids are obtained, simple molecular weights are not obtained. Morrell,⁶ for example, shows that the molecular weight of oleic acid in benzol is double the simple molecular weight, which latter however is obtained in glacial acetic acid.

An examination of the literature shows that there appears to be a conflict of evidence as to whether the molecular weights of oil-acids paralleled those of the oils from which they are prepared; *i. e.*, whether in polymerized oils the molecular weight of the fatty acid increases in the same ratio as that of the oil. Until this question can be cleared up, methods dealing with the molecular weights of the acids must be considered as useful only when no satisfactory methods for determination of the molecular weights of the oils themselves are available. The determinations on the acids necessitate, in addition, lengthy saponification, sepa-

rating and drying processes and from the standpoint of speed of working are not attractive.

In the determinations attempted in this laboratory, the freezing point method using benzol as a solvent was first tried. The method is attractive on account of its rapidity and sharpness of freezing point. Benzol is a good solvent for most oils and polymerized oils and might be expected to give satisfactory results. The apparatus used was the familiar freezing point apparatus. In all determinations benzol of a boiling point range of less than one-tenth degree was used. In Table I are given the results obtained on a number of substances by use of this method.

It is seen at once that the molecular weight of the oils in solution varies widely with the concentration. Especially in the case of polymerized oils the variations are very great. The determinations on oil acids

TABLE I—MOLECULAR WEIGHTS BY FREEZING POINT METHODS.

Substance	Benzol solvent		Nitrobenzol solvent	
	Per cent	Mol. Concentration Wt.	Per cent	Mol. Concentration Wt.
Naphthalene	0.80	126	0.61	130
(true molecular weight = 128)	1.93	125	1.38	129
Benzoic acid	0.38	202	0.54	200
(true molecular weight = 122)	1.26	217	1.41	222
	2.28	223	2.20	224
	2.78	223	...	...
Raw linseed oil	0.503	930	1.37	825
	1.32	890	3.48	845
	2.46	874	7.09	895
	3.46	864	9.75	905
	5.55	803	...	...
	8.45	740	...	...
Raw China wood oil	10.0	728	...	...
	1.5	765	...	...
	3.5	760	...	...
	6.5	740	...	...
	10.0	715	...	...
	19.5	590	...	...
Polymerized wood oil	12.2	1290	...	...
heated 45 min. at 450° F.	22.1	1025	...	...
	31.0	890	...	...
Oil acids from refined linseed oil	8.6	500	...	...
	17.2	490	...	...
	19.3	480	...	...
Oil acids from refined linseed oil	15.1	580	...	...
heated 1 hour at 600° F.	22.3	555	...	...
	33.0	520	...	...
Oil acids from refined linseed oil	6.3	780	...	...
heated 3 hours at 600° F.	19.5	755	...	...
	31.0	690	...	...

indicate that the method does not give correct results even on these substances. When the acids are obtained from raw linseed oil the molecular weight remains approximately constant over a wide variation of concentration, the value obtained being about double the simple molecular weight, but when the acids are obtained by saponifying and acidifying a polymerized oil a constant molecular weight cannot be obtained, the variations becoming more pronounced as polymerization increases.

In every case a lowering of the molecular weight with increase in concentration is observed. This is rather surprising as the reverse result might perhaps be expected. It is known, for example, that solutions of polymerized oils in many solvents show all of the

¹Comp. rend., 1802, 636-638.²Chem. Tech. and Oils, Fats and Waxes, Vol. III, pp. 98-100.³Z. angew. Chem. 19 (1906), 2698.⁴Trans. Chem. Soc., London, 101 (1912), 2082-2089.⁵Chem.-Ztg., 1907, 188.⁶J. Soc. Chem. Ind., 34, 105.

characteristics of colloidal solutions. In such solutions and in solutions in which association of the solute occurs molecular weight rises as concentration is increased. A lowering such as is indicated in Table I is generally ascribed to combination between the solvent and the solute, and until some better explanation appears this must be accepted as the cause of the phenomenon noted here.

It is possible that association does play some part in the changes observed, although it is apparently overbalanced in this case by the influence of combination. Solvents which generally possess markedly different associating powers from benzol might be expected to give interesting results. Benzol is generally accepted as an associating solvent; nitrobenzol behaves as a neutral solvent and chloroform as a dissociating solvent in ordinary molecular weight determina-

TABLE II—MOLECULAR WEIGHTS BY BOILING POINT METHODS.
Chloroform Solvent Benzol Solvent

	% Conc.	Mol. Wt.		% Conc.	Mol. Wt.
Naphthalene(a)	0.8	129	Naphthalene(a)	0.9	135
	2.7	133		3.9	137
Benzoic acid(b)	0.2	211		8.0	135
	0.63	222	Benzoic acid(b)	1.5	240
	1.75	228		3.2	252
	5.70	220		5.5	240
Alkali refined linseed oil	0.87	(c)	Refined linseed oil	1.1	2080
	2.00	1400		2.5	2780
	3.00	865		4.7	1042
	4.6	700		8.0	860
	6.0	655		10.9	765
	7.4	580		14.8	682
	9.3	472	Oil acid from lin-		
Raw linseed oil	1.3	(d)	seed oil	1.9	544
	2.9	845		4.6	540
	4.3	700		7.0	485
	5.75	625		9.8	474
	7.2	605		12.4	460
	9.3	512	W. G. Rosin	1.28	831
Polymerized lin-				4.1	650
seed oil	1.8	(e)		7.3	595
	3.6	3380		9.9	580
	5.5	1800			
	7.9	1192			
	9.8	960			

(a) True Mol. Wt. = 128. (b) True Mol. Wt. = 122.
(c) Lowered Boiling Point 0.01°. (d) Lowered Boiling Point 0.033°. (e) Lowered Boiling Point 0.07°.

tions. The two latter materials were therefore chosen for further investigation.

Determinations of molecular weight by the freezing point method using nitrobenzol as the solvent were made in the ordinary apparatus and although slight difficulty was found with excessive undercooling fairly accurate results could be obtained. Some of the observations in this solvent appear in Table I. In this case the characteristics usually ascribed to association in solution appear, that is, increase of molecular weight with increase in concentration. It is interesting to note, however, that benzoic acid increases in exactly the same ratio in this solvent as it did in benzol, while the behavior of linseed oil is exactly the opposite.

Boiling point determinations were made by suspending the boiling point tube in a Dewar bulb to insure insulation from external temperature changes, and heating the solvent to boiling by means of an im-

mersed coil of wire heated electrically. This method has been widely applied recently and has been found to give results comparable with those obtained in the older style boiling point apparatus.

The results of determinations in chloroform by this method (see Table II) indicate lowering of molecular weight with increase in concentration, although benzoic acid still behaves as though associated. The variations are even greater in chloroform than in the other solvents previously tried. The remarkable lowering of the boiling point which has been observed by Firth and Myers² appears here when low concentrations are used. In one instance, for example, it has as high a value as 0.07°. That this phenomenon occurs explains to some extent the abnormally high molecular weights observed in low concentrations.

Using benzol as a solvent, different results as regards association might be expected at boiling temperature from those observed at freezing temperature. Accordingly, determinations were made by the boiling point method in benzol. Here again (see Table II) molecular weight varies widely with concentration and the results cannot be accepted as satisfactory. It should be noted that the value of the constant used in calculating the results was somewhat in error as is shown by the high molecular weight of naphthalene observed.

It is seen from the preceding results that all the methods so far tried have given unsatisfactory results. In the search for a solvent which would give normal molecular weights, stearic acid was suggested. Stearic acid has been recommended by Biltz,⁸ who finds it a satisfactory solvent for many determinations. It is especially desirable in an investigation of the molecular weights of oils as it possesses remarkable solvent powers for the highly polymerized and highly oxidized oils which are but sparingly soluble in other solvents. It was accordingly tried as a solvent in the usual freezing point method.

It developed at once that the ordinary apparatus is not suitable as the stearic acid tends to crawl up the side of the tube and up the stirrer, giving considerable trouble. Such difficulty was readily remedied, however, by covering with asbestos paper a piece of brass tubing of such size as to fit over the top of the freezing point tube, and winding on a resistance coil of nichrome wire. By passage of a suitable current the tubing was maintained at about 60° C. By the use of this simple heater the top of the freezing point tube remains clean and free from acid throughout many determinations.

Stearic acid of commercial purity, preferably the triple pressed grade, will be found suitable for the determinations. The melting point is not quite as sharp as in the case of benzol, but it is sharp enough to give concordant results as the data quoted later will show. It is necessary first to dry the acid by heating it for some time below 100° C. in an oven

⁸Chem. Soc. Trans., 105, 2887-2892.

²Z. physik. Chem., 13, 355.

or on a steam-heated hot plate. The acid thus dried does not readily absorb moisture from the air and can be filled directly into the freezing point tube. The constant of the acid was found to be 42.5, a figure in concordance with the results reported by Biltz.⁹

Table III indicates the results of the determinations of molecular weights of a large number of substances by this method. In this method no uni-

The solvent is non-hydroscopic and the precautions which must be taken with nitrobenzol and, to some extent, with benzol, can therefore be omitted.

Some difficulties with the method have, of course, developed during its investigation in this laboratory; these in general, however, admit of satisfactory solution. For example, to obtain concordant results it is necessary to keep the bath in which the freezing point tube is immersed at approximately 40° C. Variation of more than one degree in the temperature of the bath will cause slight variation in the observed freezing point. If an automatically regulated thermostat is available that factor will cause no trouble. It is necessary to stir somewhat more vigorously than when benzol is used, in order to prevent undue supercooling. Under no circumstances are the observed freezing points sharper than one one-hundredth of a degree. On this account the accuracy of the method is not as great as the freezing point method in benzol but it compares very favorably with any of the boiling point methods.

The method as outlined clears up a number of difficulties which have been found with the determinations of molecular weights of oils and varnishes in the past and opens up the field for further investigations of this type. It has been found in this laboratory, for example, that determinations of molecular weights are of great importance in varnish control work and of even greater value in varnish analysis, for in many cases the treatment of an oil or varnish will be more accurately represented by its molecular weight than by any other of the common constants. For such application it is, of course, necessary to have at hand methods for determining the molecular weight of the various substances which make up the mixture of which the mean molecular weight has been determined by the methods indicated.

The process of determining such individual molecular weights in substances as simple as oils and polymerized oils is comparatively easy and will be outlined in full in a subsequent paper on polymerized linseed oil. Much greater difficulties arise when the molecular weight of the oil portion of a rosin-China wood oil varnish needs to be determined, but considerable progress has been made in the development of satisfactory methods. This will also be reported on later.

SUMMARY.

The question of the determinations of molecular weights of oils, treated oils and varnishes has been outlined and the value of such investigations brought out.

The most usual solvents used in molecular weight determinations have been investigated and their inadaptability to the present problem pointed out.

A method for determinations of molecular weights of these products by use of stearic acid as a solvent has been outlined and the conditions surrounding its use developed.

TABLE III—MOLECULAR WEIGHTS BY STEARIC ACID METHOD.

Substance	Per cent Concentration	Molecular Weight
Naphthalene	3.2	126
(true molecular weight 128)	9.1	127.5
Benzoic acid	2.2	120
(true molecular weight 122)	6.1	121
	10.8	123.1
Raw linseed oil	3.8	740
(chemically refined)	7.4	735
	10.2	760
Refined linseed oil	4.3	735
heated to 600° F.	7.7	770
	11.8	765
Refined linseed oil	4.1	1000
heated 1 hr. at 600° F.	8.4	1000
	12.0	1020
Refined linseed oil	3.84	1250
heated 2 hrs. at 600° F.	7.5	1220
	18.8	1240
Refined linseed oil	6.2	1510
heated 3 hrs. at 600° F.	11.3	1500
	17.1	1530
Acids from refined linseed oil	5.3	274
	14.0	300
	19.0	316
Acids from refined linseed oil	5.9	316
heated 1 hr. at 600° F.	10.0	325
	21.8	342
Acids from refined linseed oil	5.1	335
heated 3 hrs. at 600° F.	12.1	354
	19.2	380
Raw China wood oil	7.0	840
	13.5	825
	28.2	855
Polymerized China wood oil	6.5	1700
heated 45 mins. at 450° F.	14.8	1760
	21.1	1740
Soya bean oil	5.6	719
	8.1	735
	10.2	750
Polymerized soya bean oil	15.0	1250
heated 2 hrs. at 600° F.	30.0	1230
W. G. Rosin	5.9	282
	6.5	288

form variation of molecular weight with concentration is shown. In the determination of the molecular weights of oil acids slight variation does appear, it is true, but this is not as pronounced as in the case of molecular weights of oils in other solvents. It should also be noted in this connection that the molecular weights of the acids obtained are fairly close to the simple molecular weight as calculated from the combining numbers. With the possible exception noted, then, the method can be applied to routine determinations without the necessity of laboriously plotting curves showing the concentration effect for each oil used.

Owing to the great solubility in stearic acid of the various oils likely to be encountered, the method is widely applicable and, in fact, there will be but very few oils found that cannot be dissolved completely in the quantities required for a determination. The method is simple and easy to operate. No correction for loss of solvent by evaporation need be applied.

⁹Loc. cit.

Determinations by this method have been made on a large number of oil and varnish products.

The applicability and value of such a method have been indicated.

The writers wish to acknowledge their indebtedness to Dr. W. R. Veazey, Case School of Applied Science, Cleveland, Ohio, for advice and suggestions.

QUALITATIVE AND QUANTITATIVE ANALYSIS OF TUNGSTEN.*

By M. L. HARTMAN†

The directions for making the qualitative reduction test are as follows: Boil at least 0.2 gram of finely divided material in a small test tube with concentrated hydrochloric acid until about one-half of the acid is evaporated. Dilute with an equal volume of water, add a piece of metallic tin, and heat if necessary. A fine blue color in the solution, or a blue residue, indicates the presence of tungsten. If this test gives negative results, about 0.5 gram of the material should be fused in at least four grams of sodium carbonate. (This may be done with an ordinary Bunsen burner in a metal crucible or before the blast in a porcelain crucible.) Dissolve the fused mass by boiling water in the crucible. Acidify the aqueous solution with an equal volume of concentrated hydrochloric acid, add a piece of metallic tin, and warm if necessary. The volume of the solution should not be more than 10-20 cc. A fine blue color in the solution or a blue residue indicates the presence of tungsten. In either case, if reduction is continued long enough, a brown color is obtained.

These tests if properly used will show the presence of tungsten in materials as low as 2 per cent, and by using special precautions will detect tungsten in even lower grade materials.

Columbium (Niobium) is the only element at all likely to give a blue color under the conditions of this test. This blue can be distinguished from the blue of tungsten oxides by the fact that it disappears when the blue solution is diluted with water. Vanadium also gives a blue color when solutions of its salts are reduced, but tartaric acid will cause this reduction, whereas it will not reduce tungstic oxide. Molybdenum on reduction goes through a series of color changes from violet to blue to black. Titanium gives a violet color. No other elements will ordinarily interfere with the test for tungsten.

The following three methods are the ones in most common use for the quantitative determination of tungsten in ores. The first two are quoted from A. H. Low's "Technical Methods of Ore Analysis." The third is a method preferred by some analysts.

Hydrofluoric Acid Method.—Treat 0.5 gram of very finely powdered ore in a small platinum dish with

equal parts of strong HCl and HF acids. Digest on a water bath until solution is complete, adding more of each acid from time to time if necessary. It may require from one to several hours to effect complete decomposition of the ore. Usually a perfect solution may be obtained. Any tin oxide present will be unaffected. Finally, evaporate to about 15 cc. with an excess of HCl. A yellow precipitate of H_2WO_4 may separate during the final evaporation, owing to the expulsion of the hydrofluoric acid that holds it in solution. This will do no harm, provided it can be removed from the dish. Transfer the solution and any precipitate to a 6-ounce flask, add 20 cc. HCl acid and 8 cc. strong nitric acid. Boil down to about 10 cc. This will expel any remaining HF and precipitate the tungsten as tungstic acid. Dilute with 50 cc. hot water and allow to simmer at a gentle heat for about half an hour or until the tungstic acid has settled clear. Filter, wash with hot water, slightly acidulated with HCl, and then dissolve the tungstic acid on the filter by pouring warm dilute ammonia over it, using as little as possible, and washing the filter with the same solution. Receive the filtrate in a weighed platinum dish. Evaporate the solution on a water bath to dryness, and then ignite the residue at a red heat, cool and weigh as WO_3 . The cold residue should be a bright yellow color. Multiply the weight of the WO_3 by 0.793 to obtain the weight of tungsten, from which the percentage in the ore may be calculated.

Fusion Method for Tungsten Ores.—Fuse 0.5 gram of the very finely ground ore with 2 to 3 grams of sodium-potassium carbonate in a platinum crucible for from one-half to three-quarters of an hour. Dissolve the fused mass in boiling water. The tungsten goes into solution as sodium or potassium tungstate, together with alkali silicate, and also stannate, if tin is present. The residue contains the iron, manganese, calcium and magnesium. Filter and wash with hot water. Rinse the residue into a beaker, and warm with dilute HCl. If gritty particles remain undissolved, filter them off through the filter last used and wash with hot water. Dry and ignite the residue, and again fuse it with the mixed carbonates. Dissolve the fused mass as before, filter and unite the filtrate with the first filtrate.

Having thus obtained an aqueous solution of alkali tungstate, add to it an excess of nitric acid, and evaporate to dryness on a water bath. Again add a little nitric acid and evaporate to dryness a second and third time. Finally heat the residue in a drying oven at 120°C . for some time and then moisten with strong nitric acid and allow to stand for 15 or 20 minutes. Now add a hot 5% solution of ammonium nitrate and filter the mixture, washing well with ammonium nitrate solution slightly acid with nitric acid to remove all the sodium and potassium salts. Finally wash once or twice more with a hot, very dilute ammonium nitrate solution and then dry the filter and con-

*From The Pahasapa Quarterly.

†Professor of Chemistry South Dakota School of Mines, Rapid City, S. Dak.

tents and transfer the latter as completely as possible to a weighed platinum crucible. Moisten the paper with a strong solution of ammonium nitrate, dry it and incinerate over the crucible in a coil of platinum wire. Ignite the whole, now, with free access of air. If the tungstic acid is not pure yellow when cool, moisten with a few drops of nitric acid and repeat the ignition.

The ignited tungstic acid may contain silica and stannic oxide. The former may be removed by warming with a few cc. HF, evaporating to dryness and igniting. The residue consists of pure tungstic acid or tungstic acid and stannic oxide. The amount of the latter is usually so small as to be negligible. If desired, the tin may be volatilized as stannic chloride by ignition with ammonium chloride. The stannic chloride is decomposed by the moisture of the air and stannic oxide may be deposited on the outside of the crucible. To prevent this, place the crucible in a larger one, and keep the outer crucible covered until the ammonium chloride is completely expelled. Now heat the inner crucible with free access of air until its contents become of a pure yellow color. Cool and weigh. Repeat the ignition with six or eight times as much ammonium chloride as there is precipitate, until the weight of the residue WO_3 becomes constant. The tungstic oxide becomes dark on igniting in the absence of air and only assumes its true color and weight on igniting with free access of air.

The weight of the WO_3 multiplied by 0.793 gives that of the tungsten.

Aqua Regia Method.—One gram of the finely ground ore is treated with about 50 cc. aqua regia in a 4-ounce flask. The solution should be heated but not boiled, and the flask should be frequently shaken. When the solution is evaporated to 10 or 15 cc. it is diluted with 50 cc. hot water and allowed to stand for a half hour. The solution is then decanted through a filter paper, and the residue washed several times by decantation, using about 50 cc. hot water each time. The wash water should be slightly acidulated with hydrochloric acid. Add about 20 cc. ammonium hydroxide solution to the residue in the beaker and when the yellow tungsten acid is dissolved, decant through the filter paper. The ammonium hydroxide solution is best made by adding 200 cc. strong ammonium hydroxide with 1,000 cc. water and adding a little hydrochloric acid (about 10 cc.) to form some ammonium chloride. The residue is transferred to the paper by means of this solution, and washed thoroughly. The silica should be white. If it showed signs of incomplete decomposition before transferring to the paper, it should be heated with aqua regia again and treated as before. The ammoniacal solution is evaporated to dryness in a weighed platinum dish, ignited gently to drive off the ammonium salts, and finally heated strongly in the burner flame. Cool, moisten with hydrofluoric acid, and

again evaporate to dryness, ignite, and weigh as tungstic oxide.

WORLD'S PRODUCTION OF RAW SILK.

The Union of the Raw Silk Merchants of Lyon has recently made public provisional statistics for the production of raw silk throughout the world for the year 1915. The union's preliminary figures for 1914 and the corrected data for 1913 and 1912 are included in Table 1 to render comparison easy:

Countries.	1912	1913	1914*	1915*
Western Europe.	Pounds.	Pounds.	Pounds.	Pounds.
France	1,113,331	771,618	892,872	286,601
Italy	9,049,975	7,804,363	8,994,859	6,341,903
Spain	171,960	180,779	154,324	110,231
Austria-Hungary ...	648,159	601,862	672,410	368,172
Total	10,983,428	9,358,622	10,714,465	7,109,907
Levant and Central Asia.				
Asiatic Turkey:				
Anatolia	844,370	1,025,149	793,664	385,809
Syria and Cyprus.	881,849	1,089,265	925,941	771,618
Other provinces...	253,532	297,624	242,509	143,300
European Turkey:				
Adrianople	573,202	187,393	132,277	66,138
Balkans: Bulgaria, Serbia and Roumania	319,670	297,624	231,485	220,462
Greece, Saloniki, and Crete	110,231	407,855	330,693	176,370
Caucasus	870,826	848,780	771,618	275,578
Turkestan and Central Asia (exports)	568,793	496,040		110,231
Persia (exports)....	500,449	462,971		88,185
Total	4,922,922	5,103,701	3,428,187	2,237,691
Far East.				
China:				
Exports from Shanghai†	14,197,768	12,709,648	8,201,195	12,213,600
Exports from Canton†	4,982,446	6,062,711	4,287,990	4,321,060
Japan: Exports from Yokohama	23,957,631	26,720,022	21,495,068	24,802,006
East Indies: Exports from Bengal and Cashmere	370,377	249,122	66,139	178,574
Indo-China (exports)	33,069	26,456	22,046	30,865
Total	43,541,291	45,767,959	34,072,438	41,546,105
Grand total.....	59,417,641	60,230,282	48,215,090	50,893,703

*Preliminary. †Including tussahs, filatures, etc. ‡Including exports to Bombay and India.

The corrected figures of the 1914 production are: Europe, 10,670,372 pounds; Levant, 3,935,251 pounds; Far East, 34,381,090 pounds; total, 48,986,713 pounds.

Concerning the 1915 returns it must be observed that the European figures are much below those of the preceding year. Though these crops show a weakening tendency, the importance of the deficit is accidental and is due only to the state of war—to which cause is also attributable the decrease in the Levant and Central Asia. The exports from the Far East, which in 1914 had been reduced on account of the general conflagration, were almost normal in 1915; and because of this recovery the total world crop of 1915 was slightly superior to that of the preceding year.

AGREEMENTS AMONG GERMAN DYE-STUFF MANUFACTURERS.

The German Dyestuff Manufacturers have taken steps that are likely to be of far-reaching industrial importance. According to a report of the U. S. Consul at Frankfort-on-the-Main, the two important groups among the large dyestuff and chemical industries of Germany have combined in a defensive alliance. Each of these groups contains three of the more important concerns which, although operating independently, have had an understanding among themselves as to various matters arising in the conduct of their business. The groups themselves had no common interest and were active competitors. The profits accruing in one of the two groups were divided among the three concerns according to a scale agreed upon. In the other group there was no pooling of profits.

For some time past negotiations have been pending for a further combination of the two groups and the adding of other concerns thereto. It is now reported that such combination has been accomplished. The reason for a further uniting of the industry is stated to have grown in part out of the war and the heavy losses due to an interruption of business in hostile countries, to the large outstanding accounts as well as to property interests in these countries, together with proposed legislation in several countries regarding trade. References have been made in newspapers of the proposed efforts in the United States and England to establish the dyestuff industry on a large scale and thus increase competition in these countries. Proposed legislation in the United States to increase the tariff on dyestuffs and to prevent the sale of dyestuffs in the country at a lower price than the same products are sold in Germany, is also referred to. The movement now on foot among the factories is said to be merely a defensive one to meet the more difficult situation that has arisen and is likely to arise after the war. If it becomes necessary to manufacture in foreign countries, the industry acting as a whole can do this more easily than a single concern or a small group could do.

The plan as agreed upon leaves each concern an independent and competing one, with its own plant, laboratories, officers, and workmen under its entire control. A trust or a combination with the ordinary trust features is not contemplated and, it is claimed, would be opposed by all the concerns both as against their own interests and those of the industry as a whole. Arrangement is made, however, for a mutual exchange of information as to factory methods and other matters tending to reduce the cost of manufacture and otherwise strengthen the industry as a whole. The total profits are to be divided at the end of the year according to an agreed scale.

The concerns named as included in the new ar-

rangement with the capital stock of each are as follows:

Badische Anilin-und-Sodafabrik, Ludwigshafen, capital stock, 54,000,000 marks (\$12,852,000).

Farbenfabriken Friedrich Bayer & Co., Leverkusen, capital stock, 54,000,000 marks (\$12,852,000).

Farbwerke von Meister, Lucius & Brüning, Höchst-am-Main, capital stock, 54,000,000 marks (\$12,852,000).

Leopold Cassella & Co., Frankfort-on-Main, capital stock, 30,000,000 marks (\$7,140,000).

Aktiengesellschaft für Anilin-Fabrikation, Berlin, capital stock, 19,800,000 marks (\$4,712,400).

Chemische Fabriken vorm. Weiler ter Meer, Uerdingen-am-Rhein, capital stock, 8,000,000 marks (\$1,904,000).

Kalle & Co., Biebrich-am-Rhein, capital stock, 6,000,000 marks (\$1,428,000).

The dividends paid by the three first-named concerns in 1914 were 19, 19, and 20 per cent, respectively. It is expected that a dividend of 20 per cent will be paid by each for the year 1915.

For many years the value of the copper mined in the Central States has exceeded that of zinc, frequently by millions of dollars, owing entirely to the greater value of the copper, for the quantity of zinc produced has been larger. Under the stimulus of extraordinary prices for both copper and zinc in 1915 the mine output of copper in the central states increased 50,650 tons and that of zinc 47,857 tons. The value of the copper produced increased from \$21,805,043 to \$46,494,969, an unusual increase, but not sufficient to retain its pre-eminence, for the value of the recoverable zinc jumped from \$17,139,264 in 1914 to \$53,540,472 in 1915. "Jack" thus running \$7,000,000 ahead of copper. Under ordinary conditions the production of 222,548 tons of lead, valued at \$20,919,512, an increase of 18,703 tons in quantity and of \$5,000,000 in value, would have attracted considerable attention. An increase in value of one-third is unusual, but it appears small compared with that of either zinc or copper.

The U. S. Civil Service Commission announces an open competitive examination for natural gas engineer, for men only. From the register of eligibles resulting from this examination certification will be made to fill a vacancy in this position in the Bureau of Mines, Department of the Interior, for service in the field, at a salary ranging from \$1,800 to \$2,500 per annum. The duties of this position will be to participate in the engineering and economic work of the Bureau of Mines in relation to the production, transportation, distribution, and utilization of natural gas throughout the United States, and with special reference to the prevention of waste, and the improvement of methods used in the industry.

The CHEMICAL ENGINEER

PUBLISHED MONTHLY by the MYRON C. CLARK
PUBLISHING CO.,

608 S. Dearborn Street, Chicago

*Entered as Second Class Matter, Aug. 19, 1907, at the Post Office
at Chicago, Illinois, under Act of March 3, 1879.*

Subscription—United States, Cuba and Mexico \$2.00
Extra postage to Canada 25c a year; to foreign countries 50c a year.
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All communications should be sent to THE CHEMICAL ENGINEER, 608
S. Dearborn Street, Chicago, Ill.

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NOTES AND COMMENTS.

Oxidation of Automobile Cylinder Oils.

The carbonization value of oil is coming to be recognized as a valuable criterion in routine testing. For this reason a research was undertaken by the Bureau of Standards to determine the increase in carbonization value in weight, acidity, and demulsibility of automobile cylinder oils upon heating. The resulting data are contained in Technologic Paper No. 73 issued recently by the Bureau. The bearing of the work upon the testing of oils is pointed out. The changes in the Maumené and iodine numbers also were ascertained.

New School of Chemical Engineering Practice.

The Massachusetts Institute of Technology has been prompt to recognize the needs of the chemical industry. Announcement has been made that it will establish a new school of chemical engineering practice that will not only combine a regular college course but also will include actual experience at industrial plants. The school will include regular courses with a resident professor at five or six industrial plants. These stations are to be located at Somerville, Bangor,

Me.; Niagara Falls, N. Y.; Allentown, Pa., and Chicago. The course, which leads to a master's degree after five years of study, includes three and one-half years at the institute, nine months at the several industrial plants and the last nine months in the institute laboratories.

Additional Appropriation for Forest Products Laboratory.

The National Lumber Manufacturers' Association has appealed to congress for additional appropriations for carrying on experiments at the federal forest products laboratory at Madison, Wis. At the present time the laboratory is allowed \$140,000 a year, and the lumber manufacturers have asked for an additional appropriation of \$75,000 to carry on experiments in relieving the paper famine by utilizing the paper mill waste.

Dye Stuff Production in Japan.

The Mitsui Mining Co., according to the *Japanese Times*, has produced an assortment of artificial dye-stuffs at the Miike coal-tar works and some of them have just been placed on the market through the company's selling agents, the Mitsui Bussan Kaisha. Other varieties will be marketed in June. Preliminary experiments were begun at Miike by the company immediately after the outbreak of war. The series of products now placed upon the market includes alizarin reds, aniline salt, aniline oil, 90 per cent benzol, 50 per cent benzol, solvent naphtha, sulphuric acid, nitric acid, hydrochloric acid, and some other chemicals in addition to coal tar, pitch, refined naphthalene, ammonium sulphate, and a few other articles currently produced before the war. It was announced that in June alizarin maroon, alizarin blue, para-nitraniline, Congo red, fast red, and naphthol would be offered for sale.

Study of the Volatilization of Platinum.

The United States Bureau of Standards has issued Scientific Paper No. 280, in which are given the results of an investigation made at the suggestion of a committee of the American Chemical Society, on the loss in weight on heating of platinum crucibles of various makes and degrees of purity. The results obtained should prove of considerable value to the analytical chemist in aiding him to eliminate a troublesome source of error. It is shown that all grades of platinum contain at least traces of iron, that there is no appreciable loss in weight of crucibles heated to 900° C., that above this temperature the loss increases very rapidly with temperature and is greatest for platinum containing iridium and least for platinum alloyed with rhodium.

Large Increase in Production of Spearmint.

One of the features of the 1914 census of manufactures for the essential-oil industry is the largely increased output of spearmint, as shown by the figures

of a preliminary statement issued on the subject by the United States Bureau of the Census, in which a comparison is made with the statistics for 1909.

The value of the annual output of essential oils, as a group, increased by 16 per cent during the 5-year period. The production of peppermint increased 19 per cent in quantity and 15.9 per cent in value; that of spearmint increased 182.1 per cent in quantity and 185.9 per cent in value; that of black birch decreased 38.6 per cent in quantity and 33.7 per cent in value; that of wintergreen decreased 73.1 per cent in quantity and 64.4 per cent in value; and that of wormwood and other essential oils increased 5.7 per cent in value. The output of witch-hazel extract increased 32.6 per cent in quantity and 37.2 per cent in value.

The total products of this industry for 1914, as reported by 108 establishments engaged in the industry, were valued at \$2,565,361. This total comprised essential oils, valued at \$1,289,482; 917,690 gallons of witch-hazel extract, valued at \$575,938; and other products to the value of \$699,941. At the census of 1909, 74 establishments were reported with products valued at \$1,773,304. Of this amount, \$1,111,805 represented the value of essential oils, \$419,793 the value of 691,823 gallons of witch-hazel extract, and \$241,706 the value of all other products. The value of all products in 1914, therefore, was \$792,057, or 44.7 per cent, more than in 1909. These products do not include synthetic or artificial oils, of which there is a considerable production, notably of synthetic oil of wintergreen. They do include the essential-oil products of two establishments in 1914 and six in 1909, engaged primarily in other branches of manufacture.

Including the by-products and the essential oils distilled for others, the total production in 1914 comprised 363,991 pounds of peppermint, valued at \$601,617; 94,209 pounds of spearmint, valued at \$238,074; 41,178 pounds of black birch, valued at \$67,691; 6,000 pounds of wintergreen, valued at \$24,538; 4,702 pounds of wormwood, valued at \$9,040; and oils of camphor, cedar, cloves, lemon, parsley, patchouli, pennyroyal, sandalwood, sassafras, tansy, etc., to the value of \$348,522.

Visible Spectrum of Acetylene Flame Studied.

Data on the distribution of energy in the visible spectrum of a standard source of light are frequently needed in connection with investigations in physiology, in psychology, and in physics, especially in photoelectric work, in photography, and in the photometry of faint light sources. The acetylene flame appears to be a promising source of light, having a high intensity and a white color. Numerous requests having come to the U. S. Bureau of Standards for data of this type, an investigation was made to supply the information desired, and the results have been published in Scientific Paper No. 279, just issued. The paper gives data on the distribution of energy in the visible spectrum of a cylindrical acetylene flame operated under specified conditions.

THE NORWEGIAN PAPER MARKET DURING 1915.

According to the Norwegian trade paper *Tidsskrift for Papirindustri*, the year 1915 was full of surprises for makers as well as for consumers. The makers have had serious difficulties in obtaining requisites and coal. They have also experienced disagreeable surprises in regard to the cost of production. Moreover, makers and consumers agree that the high prices now being demanded and those paid at the end of the year are quite unusual.

In the first quarter of the year there was comparatively little activity. Prices were generally low and hardly profitable. The second quarter showed a considerable improvement, with a heavy demand and an unusually rapid rise in prices, while the characteristics of the third and fourth quarters were the ever-advancing prices, the full order books with all mills, and, consequently, the serious difficulties in filling the requirements of customers.

An idea of the year's fluctuations will be seen in the following prices per long ton f. o. b. Norway:

Kinds of paper.	January, 1915.	December, 1915.
News on reels.....	\$ 40.00	\$53.33-56.00
Glazed news.....	42.67	61.33
Pure kraits.....	64.00-66.67	106.67
Grease proof.....	80.00	133.33
Ordinary M. G. cap., 9 pounds.....	61.33	106.67
Glazed wood-free printing.....	93.33	133.33

As mentioned above, the cost of production has been heavily increased during the year, but not in proportion to the prices obtained now, so that those mills which are not at present bound to old contracts should now make a considerable profit.

The year 1915 can hardly be described as satisfactory from the point of view of pulp makers. Part of Norway's production was probably tied up to old contracts, the selling price of which doubtless made it difficult to make business profitable. The cost of all kinds of raw materials has been on a mounting scale throughout the year, whereas during the first nine months of 1915 selling prices kept satisfactory. When the autumn set in, prices for all kinds of chemical wood pulp became firm, and the year expired with high and rising prices and an exceedingly firm market. In the middle of December the quotations were per English ton f. o. b. South Norway: For bleached sulphite, \$86.67; easy bleaching sulphite, \$61.33; strong sulphite and kraft pulp, \$50.67-\$57.33. With navigation closed in the Baltic and supplies from Germany, Austria, and England cut off, prices should continue to be in the favor of the sellers.

Since December the prices have continued rising, and the latest quotations are now (February) f. o. b. South Norway: Bleached sulphite, \$106.67; easy bleaching sulphite, \$72; strong sulphite, \$64; kraft pulp, \$66.67.

Dry mechanical wood pulp was firm all year, with good prices. The quotation is now \$29.33. Moist mechanical wood pulp has as usual fluctuated surprisingly.

Chemical Engineer and Manufacturer

Vol. XXIV.

JULY, 1916.

No. 1.

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THE "CHEMICAL ENGINEER" BECOMES "CHEMICAL ENGINEER AND MANUFACTURER."

The publishers of this magazine have decided to broaden its field as indicated by the new name that has been adopted.

In addition to articles of technical nature, such as we have previously published, there will hereafter appear in these columns a considerable amount of what is commonly designated as "trade literature," such as prices of chemicals and chemically manufactured products, news notes relative to projected manufacturing plants, articles on manufacturing processes and devices used therein, and, in short, that variety of reading matter that savors more of a "trade" than of a "profession."

By making this addition to the class of articles heretofore published, it is believed that the chemical engineer himself will be fully as much the gainer as will be the manufacturer.

Furthermore, it is hoped thus to bring both chemical engineer and manufacturer into closer touch, very much as the civil engineer and the contractor have been brought to a closer union through the publication of such periodicals as "Engineering and Contracting."

The publishers of "Chemical Engineer and Manufacturer" also publish "Engineering and Contracting," the pronounced success and rapid growth of which seems to indicate that a similar result will follow the adoption of a similar editorial policy by this magazine.

Prior to the first issue of "Engineering and Contracting," ten and a half years ago, civil engineering was universally regarded as a highly technical profession, mainly to be occupied by the designers of public works and rarely by the builder or operators thereof. "Engineering and Contracting" at once began preaching that civil engineers should enter both the contracting field—the field of actual supervision of construction—and the operating field. It urged engineers to secure managerial positions and political positions where their engineering knowledge would be effective in producing greater economies. This preaching has proved to be so sound that thousands of civil engineers have followed it with pronounced success.

Perhaps there has been less need to urge upon chemical engineers a similar procedure. Yet, if we mistake not, there is a very large percentage of chemical engineers to whom purely technical matters have appealed much more strongly than commercial mat-

ters. We hope to be able to bring commercial features more impressively to their attention.

Manufacturers, who employ chemical engineers—or who should employ them—will find in this magazine, we hope, enough matter of a semi-technical nature to interest them more keenly in the nature of the problems that chemical engineers are called upon—or should be called upon—to solve. Also it is planned to develop through these columns a better understanding of the principles of scientific management as applied to industries involving the application of chemical science.

We shall welcome suggestions from our readers as to ways and means of better attaining the objects above outlined.

WHY HAS AMERICA LAGGED BEHIND GERMANY IN MANUFACTURING INVOLVING CHEMICAL KNOWLEDGE?

The great war has strikingly, and we believe, fortunately forced the attention of American business men upon our national weakness in industries of a chemical nature. Our chemical engineers needed no war to teach them the real situation. For many years they have bewailed it, and this magazine has itself been a voice crying in no wilderness.

In a nation that annually issues more patents than all the European nations combined, it may well be asked why Americans have permitted Germans to monopolize an industry that calls for so much ingenuity in its development. We have interviewed a number of chemical engineers employed by large manufacturing firms, putting to each the question that heads this editorial. Four of the replied are so full of significance that we give each of them in brief:

REPLY No. 1.—Lack of sufficient chemical teaching in our public schools and academies. Our banking and business leaders are usually men possessed of at least a high school training. Many of them are college graduates. Yet rarely indeed is one of them sufficiently well versed in the elements of chemistry to understand even simple chemical formulas. Show one of those men a drawing of a machine, and he can follow your explanation, and, following it, becomes interested in your plan. Show the same man a group of chemical formulas and you are talking to him in Greek; you arouse no interest. It is a principle of psychology that the imagination cannot work save by the combination of previously conceived ideas. If a man has no ideas at all on a matter, he can dream no dreams on it; without dreams, interest is never born; without interest in a subject, no financial or industrial leader is apt to foster it; without such fostering support, the chemical engineer dreams his dreams in vain.

REPLY No. 2.—Our colleges have graduated relatively few chemists and chemical engineers. Those thus far graduated have mostly been men of the purely pro-

fessional type, either with no inclination for or with no training in industrial management. The few fitted for managerial positions have speedily found them in plants already established, leaving no surplus of such men energetically striving to find places in the world by creating new industries of their own.

REPLY No. 3.—Manufacture of dyes, chemicals and most products involving chemical action, has not been encouraged by tariffs sufficiently high to insure the needed protection during the necessary development period of every new industry. Selden, the inventor of the gasoline automobile, has said that his experience as a patent attorney has taught him that it takes fully ten years for the average new device to gain a commercial foothold. He cites such great "necessities" as the telegraph and telephone, each of which almost failed commercially before the expiration of the basic patent. Yet those devices were without competition, and had to struggle only against human reluctance to back a new enterprise with adequate capital. A new chemical industry must also face this inherent reluctance on the part of capital to back it, a reluctance that is greatly accentuated where powerful competition is known to exist. Tariff protection is needed to foster chemical industries in America.

REPLY No. 4.—Publicity as to achievements in chemistry has been lacking. Americans have not generally known what marvels this science has already accomplished, to say nothing of the far greater wonders that surely are to come. Tell men that in South America there is a big unexplored river, that you believe gold will be found in its sands, and many men will willingly finance an exploratory expedition. They will gamble for the pure fun of gambling. Adequate publicity as to the possible riches that await chemical research intelligently conducted, would arouse the gambling instinct sufficiently to secure backing for many a worthy enterprise. Chemists have discussed among themselves not only their great achievements of the past but the far greater ones to come, which their eyes can already discern as being within the realm of possibility. This has not sufficed, for they have failed to secure adequate publicity for their ideas in general magazines and newspapers.

SUMMARY.—In these replies to our editorial query we have these four reasons for American backwardness in chemical industries:

1. Lack of chemical teaching in public schools, resulting in absence of interest in chemical matters on the part of commercial and financial leaders.
2. Insufficient number of chemists and chemical engineers.
3. Inadequate tariff protection.
4. Almost no publicity to arouse general interest in chemical research.

We may add that so dense is the general ignorance on chemical matters that few people of "education" know that one of the branches of the great engineering profession is chemical. Indeed even engineers fre-

quently show that if they ever knew they have forgotten that there are chemical engineers. Vide some of the discussions of civil, mechanical, electrical and mining engineers.

Chemical engineers and manufacturers are both equally concerned in arousing public interest in this great branch of engineering. The chemical societies should begin a systematic publicity campaign through the columns of the daily papers and general magazines. They should tell, in popular style, about the recent achievements in chemistry. They should picture the future, showing what chemists believe to be susceptible of accomplishment. Our petroleum is fast vanishing. What may the chemist do to fill the automobile tank when gasoline is gone? Our coal is also vanishing. Will chemists be able to convert the great solar energy into briquettes of solid sunshine? Even our soil is losing its fertility. How will nitrogen and potash be supplied by the art of chemistry? Mechanical invention has increased the productiveness of the farm hand four-fold. How will chemical invention outstride our American plowing, sowing and harvesting devices?

Having awakened public interest in this field, big with engineering and chemical possibilities, we may confidently predict a rapid realization of many a grand, but as yet vague, dream.

New Penetration Needle for Testing Bituminous Material.

A new penetration needle for use in testing bituminous materials has been designed by Chas. S. Reeve, chemist, and Fred P. Pritchard, assistant chemist, U. S. Office of Public Roads. The following description is given in the *Journal of Agricultural Research*: The needle is made by placing a 2-in. length of 0.041 in annealed-steel drill rod in the chuck of a high-speed lathe, and by means of a fine sharp file turning the end to a sharp point having a $\frac{1}{4}$ -in. taper. When it has been made as smooth and sharp as possible by this means, the needle is tempered, then ground to a sharp point with a good stone, after which it is smoothed and polished with emery dust, crocus cloth and rouge, and finally held carefully on a buffing wheel. The finished needle should be sufficiently smooth and sharp to enter and pass through a piece of ordinary writing paper without sticking or friction. The important thing is to have the taper straight, beginning $\frac{1}{4}$ inch from the end and the needle above the taper exactly 0.04 inch in diameter.

The annual statement of the Geological Survey on graphite in 1915 is now available for distribution. According to this report, 4,718 short tons of natural graphite, valued at \$429,631, was sold during the year.

PRACTICAL ANALYSIS OF SOAP.

By M. R. DICKSON, Ph. G.*

Perhaps no other branch of industrial or experimental chemistry offers a wider or more interesting field for experiment and investigation than that incident to soap manufacture. Various fats and oils with their respective saponification values, glycerine yield, adaptability to the making of certain classes of soaps, also kinds and strengths of lye best adapted to each—all offer a very alluring field for investigation.

After several years of practical and experimental work on the subject I will give here a fairly thorough as well as an accurate and rapid working method for the analysis of a sample of soap such as would ordinarily come before the analyst.

In the main, nearly all samples should be treated the same during the preliminary steps, but as fillers, rosin, etc., are found, these receive the proper qualitative and quantitative tests. As the prices of raw materials advance the trend of the manufacturer is in at least one of three directions, namely: to cut the weight, to increase the price, or to add cheap fillers. The latter course necessarily gives new and increased problems for the analyst but none the less interesting.

Sampling.—From an ordinary cake of soap make a cross section near the middle and from this prepare the sample by cutting into fine strips or little cubes and mixing thoroughly in order to have the sample uniform. This procedure is quite important as naturally the outer surface of the cake will not contain as much moisture as the center. From the sample thus prepared carefully weigh three portions, as directed below.

Fatty-Acids, Total Alkali and Salt.—Weigh off and place in a 200 cc. beaker, 3 Gm. of the prepared sample. Add about 75 cc. or 100 cc. of distilled water and heat until dissolved. Now decompose with sulphuric acid using 50 cc. of N/2 solution accurately run from a burette. Now add 5 Gm. of clean dry stearin or wax and heat the whole until the fatty-acids and wax are melted and form an even layer on the surface. It is well at this point to boil for a few minutes, with occasional stirring, to liberate any carbon-dioxide which may be present as carbonates. Now remove the beaker and contents from the heat and place in a cool place or bath of ice-water, taking care to wash down the sides of beaker with hot water, after which avoid jarring or shaking until cool and the fatty-acid and wax have become solid. The solid cake may then be lifted out, rinsed and dried between filter papers and weighed. This weight minus 5, the number of Gms. of wax used, divided by 3, the number of Gms. of soap taken, multiplied by 100, gives the per cent of fatty-acids in the sample.

Total Alkali.—The solution remaining in the beaker is poured carefully into a 200 cc. graduated flask,

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rinse the beaker several times with distilled water. Make up to the mark on the flask, shake and filter through a dry filter, discarding the first 10 or 20 cc.

With a 25 cc. graduated pipette measure 25 cc. of the filtered liquid into a flask (about 100 cc. capacity), making two such portions, and if borax is present (as shown by having made a previous borax test), three such portions of the solution.

To the first portion add methyl-orange as an indicator and titrate back the excess acid previously added, with N/2 sodium hydrate solution. Multiply the number of cc. of N/2 sodium hydrate solution used by 8 (as you are working with but $\frac{1}{8}$ the original solution), subtract this product from 50, the number of cc. of N/2 sulphuric acid used, which will give the number of cc. of N/2 sulphuric acid required to neutralize the total alkali in the 3 Gms. of soap. Multiply this number by 0.0155, divide by 3 and multiply by 100, which will give the per cent of total alkali as sodium-oxide.

To the second portion of the solution add phenolphthalein as an indicator and then add from a graduated burette N/2 NaOH till the pink color appears, making it disappear again by the addition of one drop of N/2 sulphuric acid. Now add a little potassium chromate and titrate with N/2 silver nitrate solution until a permanent red precipitate or color is formed. Note the number of cc. used, multiply by 8 and this product by 0.005806, divide by 3 and multiply by 100 which gives the per cent of salt in the sample as NaCl.

To the third portion of the solution add phenolphthalein as an indicator and titrate with N/2 NaOH till a permanent rose red color appears. Now add about 2 or 3 Gms. of pure neutral glycerine which will cause the rose color to disappear by the formation of an acid between the glycerine and borax. Boil for ten or fifteen minutes, cool and titrate with N/2 NaOH till color reappears, noting the number of cc. of N/2 NaOH required to cause the color to reappear. Multiply this number by 8, this product by 0.0504, divide by 3 and multiply by 100. The result indicates the per cent of borax present in the sample.

Free Alkali, Silicate and Insoluble Matter.—Weigh 3 Gms. of the sample of soap into a wide mouth alkali flask of about 150 cc. capacity. Add about 50 cc. of neutral alcohol 95%, cover with a watch glass and heat on a water bath. The soap and any free caustic which may be present dissolve in the alcohol while the carbonate, silicate, and insoluble matter remain undissolved. Filter through a heated filter, preventing the soap from becoming solid, and wash flask and filter with several successive portions of hot alcohol. If there be any insoluble matter present (which will have appeared in the aqueous solution for fatty-acid test) the filter in this operation should be previously dried at 100° C. for 2 or 3 hours, cooled in a desiccator and weighed. After thoroughly washing in alcohol the filtrate (the alcoholic soap solution) is titrated with N/2 HCl using phenolphthalein as indica-

tor. The number of cc. of N/2 HCl used, multiplied by 0.0155, divided by 3 and multiplied by 100 gives the per cent of free caustic alkali as Na₂O.

The filter containing the carbonate, etc., is exhausted with hot distilled water, dried for two or three hours at 100° C., cooled in a desiccator and weighed for insoluble matter and the percentage computed. From this sample, tests may be made for the character of the insoluble matter.

The aqueous solution is divided into two equal portions.

"No. 1" is placed in a porcelain evaporating dish, made acid with dilute hydrochloric acid, and evaporated to dryness on a steam or water bath. Then is added 25 to 40 cc. of diluted hydrochloric acid and run through a previously dried, cooled, and weighed filter. Wash with hot water, dry, cool in a desiccator and weigh as silica. Multiply by 2, compute the per cent and report as "silica as silicate." Take one-quarter this per cent (approximately) and report as "alkali as silicate."

"No. 2" solution is placed in a small flask or beaker and titrated with N/2 HCl, using methyl-orange as indicator. Multiply the number of cc. of N/2 HCl used, by 2 (as we are working with but half the solution), and multiply this product by 0.0155, divide by 3 and multiply by 100, which gives the per cent as Na₂O. From this deduct the amount reported as "alkali as silicate." The remainder, which is the alkali carbonate expressed as Na₂O, is multiplied by 1.7 which gives the alkali in terms of Na₂CO₃, which is as it exists in the sample of soap.

Now from the per cent of total alkali, Na₂O, previously found, deduct the free alkali as caustic, carbonate, etc., in terms of Na₂O which gives the per cent of combined alkali, or the alkali in combination as real soap.

Moisture, Unsaponified, and Unsaponifiable.—Weigh onto a watch glass 5 Gms. of the finely cut sample and dry at 100° C. until there ceases to be loss of weight. Compute this loss in weight to per cent and report as moisture.

For unsaponified fat and unsaponifiable matter use the above dried sample, break up finely or powder, place in an extraction apparatus and extract for about two hours with petroleum ether distilling below 80° C. Distill the petroleum ether from the receiving flask, which has previously been tared, and weigh the residue as unsaponified fat and unsaponifiable matter. To determine if there be any unsaponified fat, run into the flask containing the extracted matter, accurately from a graduated burette about 10 cc. of alcoholic caustic potash (30 Gms. to the liter). Heat on a steam or hot water bath for about an hour and titrate with N/2 HCl, using phenolphthalein as indicator. At the same time run a blank test by using the same number of cc. of the alcoholic potash in a clean flask and titrate with N/2 HCl same as above. If the test shows that in the first case there has been any of the

potash absorbed (indicated by not requiring so much $N/2$ HCl to neutralize) this will indicate that there was uncombined or unsaponified fat present.

Most of the ordinary yellow laundry soaps contain varying proportions of rosin which in the analysis separates and is weighed with the fatty acids. After determining if rosin be present, by Gottlieb's or any other qualitative test, I have obtained best results in determining the percentage by following mainly Hubl's Quantitative Determination which is as follows:

Rosin.—Weigh $\frac{1}{2}$ to 1 Gm. of the solid mixture of fatty and rosin acids into a closed flask and heat on a water bath in 20 cc. of alcohol to complete solution. Neutralize this alcoholic acid solution with an alkali solution using phenolphthalein as indicator. Pour this alcoholic soap solution into a beaker of about 40 cc. capacity and make up to about 200 cc. with warm distilled water, rinsing the flask well, add silver nitrate solution till precipitation is complete. The precipitate which consists of the silver salts of fatty and rosin acids must be protected from sunlight. Filter, wash the precipitate thoroughly with warm water, dry at 100° C., and extract with sulphuric ether in an extraction apparatus.

The silver resinsates dissolve in ether, while the silver salts of the fatty acids remain undissolved. The ethereal solution of the resin salt should have a yellow or light brownish color. Add dilute hydrochloric acid and shake well in a separating funnel until the precipitation of silver is complete, separate out and wash the ethereal solution in distilled water. Finally draw off the ethereal solution of rosin into a dried dish (a wide mouth flask is good as the rosin creeps up and over the edge of an evaporating dish).

TABLE I.
WHITE LAUNDRY SOAP.

	Per cent.
Fatty acids	50.27
Rosin	0.00
Unsaponified	0.00
Unsaponifiable	0.17
Free caustic (Na_2O)	0.02
Free carbonate (Na_2CO_3)	2.99
Combined alkali (Na_2O)	6.89
Alkali as silicate	2.33
Silica as silicate	9.33
Salt ($NaCl$)	0.39
Water insoluble	0.00
Moisture	27.28
Undetermined	0.33
Total	100.00

ROSINED SOAP.

	Per cent.
Fatty acids	31.17
Rosin	19.83
Unsaponified	0.00
Unsaponifiable	3.07
Free caustic	0.00
Free carbonate (Na_2CO_3)	3.93
Combined alkali (Na_2O)	6.59
Alkali as silicate	1.21
Silica as silicate	4.87
Salt ($NaCl$)	0.28
Water insoluble	0.34
Moisture	28.43
Undetermined	0.28
Total	100.00

Evaporate off the ether, dry a short time at 100° C. and weigh the residue as rosin. As the rosin is weighed in hydrated form multiply the weight by the factor 0.9732 to obtain the weight as anhydride.

Note.—Another advantage of using a wide mouth flask for evaporating the ether is that it may be connected to the empty extractor and condenser, thus saving the ether for future use.

The reports on analysis of two well known brands of soap, one a good grade of white laundry soap, the other a heavily resined soap, are given in Table I.

Soap Industry in the United States.

The total value of the products of the soap industry in the United States increased from \$115,455,172 in 1909 to \$135,340,499 in 1914, while the number of establishments decreased from 526 to 513. Substantial increases in the five-year period were reported for hard soaps, according to a statement issued by the United States Bureau of the Census. The quantity of soft soap manufactured decreased 5.1 per cent, but its value increased 33.7 per cent. The quantity of glycerin decreased 3.2 per cent, but its value increased 11.8 per cent.

Of the 513 establishments in 1914, the principal business of 371 was the manufacture of soap and 142 were engaged primarily in other industries, such as slaughtering and meat packing and the manufacture of food products, cottonseed products, and patent medicines and compounds, and produced soap as a subsidiary product. Of the 526 establishments in 1909, the principal business of 420 was the manufacture of soap and 106 produced soap as a subsidiary product.

The total production of glycerin by all establishments in 1914, so far as it can be ascertained, not including that made and consumed in the same establishment, was 75,218,292 lbs., valued at \$13,052,240, as compared with 81,905,915 lbs. in 1909, valued at \$11,752,562. The hard-soap output increased from 1,794,249,000 lbs., valued at \$91,054,466, in 1909, to 2,064,228,000 lbs., valued at \$104,500,542, in 1914. The 1914 product comprises 938,447,000 lbs. of tallow soap, 42,524,000 lbs. of olein soap, 111,063,000 lbs. of foots soap, 169,926,000 lbs. of toilet soap, 367,744,000 lbs. of powdered soap, 97,746,000 lbs. of soap chips, and 336,778,000 pounds of other kinds of hard soap. The production of soft soap as reported in 1914 was 57,002,000 lbs., valued at \$1,607,424, and in 1909, 60,037,000 lbs., valued at \$1,269,187. In addition, there were reported special soap articles, such as soaps for technical purposes and liquid soap, to the value of \$832,654 in 1914, and \$706,177 in 1909.

According to the annual statement of the Geological Survey on fuel briquetting in 1915, now available for distribution, the production during the year was 221,537 short tons, valued at \$1,035,716.

THE MASON CITY, IOWA, PLANT OF THE NORTHWESTERN STATES PORTLAND CEMENT CO.

The Northwestern States Portland Cement Co. has erected recently at Mason City, Iowa, Portland cement mills of an annual capacity of about 2,000,000 bbls. The plant is to be erected according to the Cowham system. In it are indicated the many changes and improvements that the Portland cement industry has undergone by the adoption of economical machinery, etc. The following description of this plant and its operation are taken from a paper by Geo. P. Diekmann, chief chemist of the company, presented before the Minnesota local section of the American Society of Mechanical Engineers, and printed in the May Journal of the society.

The materials used at Mason City are limestone and clay, which are found in almost perfect composition in the vicinity. The quarry, which is only a few hundred feet away from the plant, has a limestone averaging about 97 per cent pure carbonate of lime, and many acres of it are owned by the company. The physical characteristics of this quarry are a very important feature. It has not only horizontal seams, but vertical seams at right angles to the others, and the seams are so close that the rock is in reality a multiplicity of small cubes, and very little blasting is necessary to tear them asunder.

A large steam shovel with a 3-yard dipper is used in loading this rock in side open cars that are hauled by a Shay locomotive to the plant. The stone is dumped into a receiving hopper of a gyratory crusher, which crushes the rock to a 4 in. cube size, and from here it is elevated to the top of the crusher building and again crushed by two small crushers to cubes about 2 in. and finer. The stone then passes into a set of rolls, which crushes it to about $\frac{1}{2}$ in. size and finer. The crushed material is next discharged into the bottom run of a 24 by 32 in. McCaslin conveyor which encircles the stone drying, stone crushing and stone storage building like a belt. The stone storage building has a capacity of about 30,000 tons of stone. The top run is located in the monitor of the building, and the bottom run is located in a tunnel under the storage pile. The conveyor permits of delivering the stone directly from the rolls to the dryer bins, or into the storage building.

As it is necessary to dry the stone before further reduction in size is made, this is done by two rotary stone dryers into which the stone is fed from the stone bins by Gates oscillating feeders. Each of these dryers consists of a fire-brick-lined cylindrical steel shell, 6 ft. diameter by 60 ft. long, mounted on two sets of carrying mechanisms. They are set on a slight slope, with the feed end a little higher than the discharge end; and the furnace is located at the lower, or discharge end. The heat comes into intimate contact with the particles of stone as the dryer has shelves

in it which raise the stone and shower it through the heated air and gases passing through the dryer.

From the dryers the stone is elevated and discharged into eight steel bins, from which it is discharged by means of feeders into Krupp ball mills. These ball mills take the output of the crusher above described and reduce it to coarse grit of which 50 per cent will pass through a 100 mesh sieve. This mill consists of a drum of a diameter about double its length, filled with 5,000 1-lb. steel balls, and the lining is made up of over-lapping steel plates which form steps or shelves on the inside. This drum revolves at a speed of about 26 r.p.m.

The clay fields are located about $1\frac{1}{2}$ miles southwest of the plant. No stripping is necessary as the clay is suitable directly beneath the grass roots. A specially designed plow drawn by a traction engine is used to plow this clay to the depth of about 1 in., so that the air and sun can get a chance to dry it out. The clay fields are kept higher in the middle than at the edges in order to have easy drainage.

The clay is gathered by means of a specially designed gathering machine on scrapers (revolving cylinders), each drawn by a team of horses, which load automatically. When loaded the team is driven over a bridge under which the clay track runs and the clay is dumped automatically through an opening into side-dump cars. When a certain number of cars are loaded the train is hauled to the plant and up onto a trestle, where the cars are dumped in a few seconds. The clay is then discharged, by means of a belt, into clay pans, where the grinding of the clay takes place. From here it is raised into an elevated bin, from which it is fed into the rotary clay dryers, which are similar to the stone dryers. After drying, the clay goes either to the clay storage room or to the mixing station into a steel mixer alongside the stone mixer. The clay storage has a capacity of about 15,000 tons of clay. There is also another large clay storage building at the clay fields, holding approximately the same amount of this material.

In the meantime, while these materials are being prepared, samples have been taken at every step at certain intervals and tested at the laboratory, and the chemist, knowing the composition of the limestone and of the clay, is now in position to direct the proper amounts to be mixed to obtain the proper raw mix. The ground stone and the finely divided clay are stored in adjoining bins of steel, and steel spouts lead the materials through shut-off gates to steel hoppers mounted on scales. There are two sets of scales, each of which is so arranged that the weighman can see the poise but cannot tamper with the weights, as the scale beams are in a box which is locked and the key held by the chemist on watch; the adjustment of these scales is tested very often by the chemist. The stone is weighed first and then the clay is run in on top of the stone—approximately 9,000 lbs. of the two materials is weighed per batch.

After passing through a rotary mixer this material is conveyed to Allis-Chalmers tube mills for a finer grinding and mixing. These tube mills are steel cylinders 5 ft. in diameter by 22 ft. long, supported at each end by trunnions, and filled about one-half full with flint pebbles imported from Deunmark, which are about the size of one's fist. The mixture is ground to a fineness such that about 97 per cent will pass through a 100 mesh sieve.

The raw mix, now prepared to its necessary fineness, is conveyed and elevated to the kiln building, where the raw mixture is calcined, and after all the carbon dioxide is driven off, the acid and basic constituents are fused, forming tricalcium silicates. The fusion takes place at about 2,800° Fahr. The clinker, as the fused mixture is now called, drops from the kilns into a pit and is conveyed to the clinker cooling station. The kilns are similar in their construction to the stone and clay dryers mentioned heretofore, except that they are larger. These large cylinders, which are constructed of sheet steel 9-16 in. thick and lined with fire-brick, are supported at a slight incline from the horizontal by means of rolled steel tires, each of which revolves at about one-half a revolution per minute on four heavy cast steel rollers mounted in pairs on a rocker. Each of these kilns weighs, with its load of fire-brick and charge of mix, approximately 175 tons.

A large amount of coal is used for fuel in these rotary kilns, which after being dried and powdered in suitable grinding machinery to a fineness of about 97 per cent through a 100 mesh sieve, is conveyed to steel hoppers in the rear of the kiln building, and then fed through pipes into the lower ends of the revolving cylinders and blown with a pressure of 4 oz. per sq. in. through 5-in. pipes.

The cooled clinker is next conveyed and elevated to the Kent mill building, where the clinker is reduced to the size of fine sand. This fine clinker passes over a series of screens separating the coarser clinker from the fine clinker. The fine clinker goes on to the gypsum station, while the coarser is conveyed back to the Kent mill for regrounding. The finely ground clinker passes into a hopper having a capacity of five barrels, to which a weighed amount of gypsum is added. There are two of these hoppers, to allow feeding and discharging alternately. By this process the addition of gypsum is uniform at all times, as the clinker is weighed and the gypsum weighed also, insuring perfect uniformity.

The clinker with the addition of gypsum is then elevated and conveyed to the finish tube mills, which are similar to the raw mix tube mills. Here the clinker is ground to the desired fineness, which is on the average of about 96 to 97 per cent through a 100 mesh sieve. Tests of fineness of the cement are made from each mill every hour before the cement enters the warehouse. At this point samples of the cement are delivered to the laboratory each hour for the gen-

eral tests of fineness, setting time and soundness. The warehouses in which the finished cement is stored have a capacity of 600,000 barrels.

After the cement has been tested for the necessary tests already mentioned, with the addition for tensile strength, the cement is then discharged from the warehouse bins into a conveyor running in a tunnel underneath the bins and elevated to bins above the packing machines, where the cement is packed in bags ready for shipment. Samples are taken during the loading of each car of cement and tested again at the laboratory before the car leaves the yards. The samples of cement are kept on file for six months. Perfect records of shipments and tests are kept in the laboratory, where they can be referred to.

The entire building equipment of the Northwestern States plant covers an area of about 40 acres of ground, and the buildings on the plant proper are arranged in a unique order, so that the material always advances from the crushing end through the various departments until it arrives at the packing room, where it is loaded onto the cars. About 1,600 carloads of machinery, materials, etc., of construction (exclusive of sand, gravel and crushed rock) were used in the building of this plant. The plant as it is today represents an actual cash investment of \$2,750,000, and the daily capacity is 6,000 barrels of cement.

Tanbark Output and Prices in Pennsylvania.

It is estimated that this year's cutting of tanbark in McKean, Warren, Forest and Elk counties, Pennsylvania, will amount to at least 100,000 cords. In Warren County the Central Pennsylvania Lumber Co. will peel 25,000 cords, while in Elk and Forest counties like amounts will be cut. In the vicinity of Port Alleghany and Betula in McKean county, 25,000 cords will be cut, which will be made by the Elk Tanning Co., which operates about 20 tanneries in this section. Last year the leather manufacturers were paying \$10.50 a cord, the price offered at present is \$13 a cord. It is interesting to note that 20 years ago hemlock bark in this section sold at \$4 per cord, and the trees were chopped down only for the bark, and in most cases they were left in the woods to rot instead of being hauled to the saw mills.

Chromic Iron Ore Report.

The annual statement of the Geological Survey on chromic iron ore for 1915 is now available for distribution. During the year chromic iron ore valued at \$36,744 was mined, an increase of \$28,020 over 1914. The greatly increased demand for domestic chromite, consequent upon conditions abroad, has resulted in a largely augmented production of chromite at many places in California. Until lately California has been the only producing State, but within the last few months production has commenced in southwest Oregon, near Grants Pass and Riddle.

REFINING VEGETABLE AND ANIMAL OILS.*

By CHARLES BASKERVILLE,

The terms "fat" and "wax" are commonly applied, more or less indiscriminately, to solid substances which have a greasy feeling to the touch and do not dissolve in water. Physically, waxes are regarded as having generally a harder consistency than fats. Chemically, fats are usually compounds of the trihydric alcohol, glycerol, $C_3H_5(OH)_3$; while the waxes are compounds of monohydric alcohols of large molecular weight; for example, cetyl alcohol, $C_{16}H_{33}OH$; myristic alcohol, $C_{14}H_{27}OH$, and cholesterol, $C_{27}H_{45}OH$. The names applied to some of these substances do not lessen the confusion; for example, "wool fat" and "spermaceti" are compounds of cholesterol and cetyl alcohol, hence are in reality waxes; while "Japan wax," a compound of glycerol, is actually a fat.

A fat, such as indicated above, has among other physical properties a characteristic melting-point. Those which are liquid at ordinary temperatures are called *oils*. It is of such substances more especially that this communication deals with, although reference will be made to coconut oil, which may or may not be a solid at ordinary temperatures, therefore technically might be regarded as a fat.

It will be understood that the term "oil," as here used, is not to be associated with the natural or petroleum oils, i. e., hydrocarbon oils, or the essential oils, both classes of which in general exhibit in a way the physical but not the chemical properties, necessarily, referred to above.

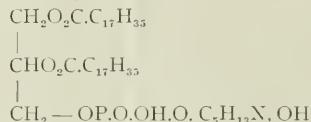
Fats are widely distributed in the vegetable and animal kingdoms, and, referring to the former only for the time being, we may say they are primarily glycerides of oleic, palmitic, and stearic acids. These fats are found mainly, but not necessarily, in the reproductive bodies, such as spores and seeds. They are found in spores, sexual and asexual, of many algae. In angiosperms they are widely distributed, replacing, wholly or in part, carbohydrates as reserve food material, and they are often associated with protein reserves; for example, in the seed from which colza oil, palm oil, cotton-seed oil, linseed oil, olive oil, and cocoa butter are obtained. It is present, perhaps, as a reserve food material, associated with starch, in some tubers. The starch in the parenchyma of the stem of certain plants may be converted into fat during the winter's cold, and vice versa, when there is a rise of temperature in the summer time. Without venturing into the misty etiology involved, we may, for our purposes, realize the likelihood of the presence of carbohydrates, proteins, and other substances derived therefrom, as gums, etc., in oils obtained

from these sources by the various means to be referred to later.

These oil-containing bodies invariably contain some coloring matter. Some of the coloring matters appear to be essential for certain of the changes just referred to. The most prominent pigment appears to be chlorophyll, an ester of tricarboxylic acid, chlorophyllin, $C_{31}H_{39}N_4Mg(COOH)_3$, and is the normal green coloring matter of plants. It may easily be broken down into substances that contain magnesium and substances that do not contain that metal.

Accompanying the chlorophyll are several pigments more or less insoluble in the cell sap; namely, carotin ($C_{40}H_{56}$), yellow to red in color, and xanthophyll ($C_{40}H_{36}O_2$), a neutral body, yellow to orange in transmitted light. These substances may be destroyed by the action of such powerful chemical agents as concentrated sulphuric acid, especially if heated in the presence of oxygen.

Closely related to the fats is a group of substances known as phosphatides or lecithins. Occurring in egg-yolk to about 9 per cent, we find them to the extent of from 0.25 to 1.75 per cent in cereals and leguminous seeds, hence they appear in the oils extracted from the seed. They are glycerol esters, two of the acidities being neutralized by fatty acids, the third being saturated by a combination of phosphoric acid and choline, as shown here.



It is easily broken up by lipase, and hydrolyzed by boiling with alkalis and acids.

We always also find a small quantity of unsaponified residue in fats, which is in the main composed of the monohydric alcohols, cholesterol, $C_{27}H_{45}OH$, and phytosterol, the latter now being a generic term for a group of allied substances, with formulas varying from $C_{27}H_{45}OH$ (sitosterol) to $C_{30}H_{47}OH$ (stigmastosterol). Cholesterol occurs in the bile, brain, and blood of animals, and is the chief alcohol constituent of wool-fat. All vegetable fats contain phytosterol, the amount varying from 0.1 to 0.3 per cent, being even higher in the oil obtained from certain peas and beans, especially Calabar beans.

The oils are extracted by disintegration of the mass involving a disruption of the oil-sacs: (a) with a suitable solvent; (b) rendering by heat, with or without water; (c) or pressure, mechanical, applied when the mass is cold or hot.

If the mass extracted be selected and perfectly clean and fresh, the oil or fat obtained is usually neutral and "sweet." The exigencies of commercial operation do not admit of these conditions, however, so the oil or fat produced is usually acid and more or less contaminated. The contaminations may be quite normal and natural. They may be bacterial in nature

*Paper presented before the Franklin Institute and printed in the June Journal of the Institute.

†Professor of Chemistry and Director of the Laboratory, College of the City of New York.

and also contain the very interesting substances known as enzymes (lipase, for example) which induce hydrolysis; that is to say, they will cause any water present to disintegrate the fats (and other bodies) into simpler bodies. This may be facilitated by exposure to air and light, so that a freshly-expressed oil that is sweet may soon acquire an unpleasant taste and odor. In some cases we say it becomes rancid, but in all cases the oil develops acidity, and the amount of the acidity of a particular oil is a function of time.

Under favorable conditions—and they are usually favorable—these changes take place within the oil-containing bodies, so that freshly-produced oil is usually acid, which acidity increases on keeping. The enzymes are “killed,” or decomposed, or at least their directive activity ceases, when they have been exposed to a temperature of about 200° C. It has not been considered a good procedure by the practitioners of the art of oil extraction and refining, however, to heat the oil to such a temperature immediately after its production; but I venture the opinion that the increased development of acidity in crude oil in storage or in transit to a refinery will be materially affected by such treatment. However, it will be necessary to be assured that substances charred or scorched at that temperature are absent.

As mentioned above, oils and fats are primarily glycerides of the saturated palmitic ($C_{16}H_{32}O_2$) and stearic ($C_{18}H_{36}O_2$) acids, associated with the fatty acids of several unsaturated series. For example:

1. Oleic acid, $C_{18}H_{34}O_2$, type $C_nH_{2n-2}O_2$.
2. Linoleic acid, $C_{18}H_{32}O_2$, type $C_nH_{2n-4}O_2$.
3. Linolenic acid, $C_{18}H_{30}O_2$, type $C_nH_{2n-6}O_2$.
4. Clupanodonic acid, $C_{18}H_{28}O_2$, type $C_nH_{2n-8}O_2$.
5. Ricinoleic acid, $C_{18}H_{34}O_3$, type $C_nH_{2n-2}O_3$.

The last is an hydroxy acid, which undergoes a particular polymerization under suitable conditions.

Most fatty oils, on exposure to the air, tend to thicken, due partly to oxidation and partly to polymerization, or both. Oils are, in fact, classified by many according to their drying qualities and tendency toward resinification. These properties play an important part in their utilization in the arts; and their treatment in refining is materially affected by the time which may have elapsed from actual production to their refining. For example, a freshly-produced linseed oil may be profitably refined by a process which is inapplicable if the oil be “aged oil.”

Oil, as stated, is normally a liquid, and we usually associate the phenomena of solution with a liquid. To be sure, this is a restricted conception, but will answer for our purposes. In this connection oil acts like water as a fluid. Water in motion carries fine particles suspended through long distances and deposits them in time, when fairly quiet, as we know from the formation of alluvial soils. Water carries certain substances in solution. These latter substances are sometimes colored and are partly fixed on

the filter when that water passes through certain filtering media. For instance, we are able to absorb Congo red from a water solution with filter-paper. Again, water carries certain substances which do not stop on the filter; they are invisible and show themselves only when we apply the ultra-microscope. These finely-divided substances, not small enough to be in actual solution, will remain suspended in the water for long periods of time. They are called colloids. By various means, through heat, addition of an acid, an alkali, or a salt, by the influence of an electric current, or by the addition of other colloids, these very finely-divided substances may be caused to agglomerate; that is, they may be converted into particles of sufficient size to be separated from the fluid by means of a filter. Exactly the same is true of oils. Organic colloid solutions may be viscous; the liquid particles are suspended in a liquid medium.

Many of the contaminating substances, referred to here in general, may be suspended in the oil, may be in solution in the oil, or may be in a colloidal condition in the oil.

It will, therefore, be quite apparent that crude vegetable and animal oils contain a variety of impurities traceable to a great variety of causes. The character of the crude oil depends not only upon the kind and part of the vegetable (wood, nut, seed, etc.) and animal (fish, whale, etc.) used, but the quality of the raw material at the time of expression or extraction (rusting, rotting, fermentation, sprouting, heating, etc.), the method followed, the care exercised in the process, and the conditions to which the oil is subjected prior to its refining. In many cases, in fact, we find metallic soaps present in the crude oil, which soaps have resulted from an interaction of decomposition products of the oil and the rendering vessels.

No universal method for refining animal and vegetable oils is known. Your forbearance will not be taxed, however, even were it profitable, in discussing all the various proposals for fitting these oils best to the several purposes experience and practice have shown them to be applicable. A number of processes have been proposed, patented, or kept secret during the last 125 years. Around the knowledge and power of the practical oil-refiner not a little mystery still obtains. Each individual oil presents its own problem, and even the same oil by name, obtained under different conditions, involves judgment, based on the knowledge of the chemistry involved, to secure the best and most economical results. Furthermore, the use to which the oil is to be put must be considered; for example, one wants acid oil for some paints and neutral oils for foods.

Some four general methods of refining oils have been and are being worked in practice. They are:

1. Treatment with steam (plain or superheated) whereby some coagulation results and many odoriferous substances are driven off. This does not diminish the free fatty acid content of the oil so treated.

2. Treatment with variable amounts of concentrated sulphuric acid (Gower, 1792) under determined conditions of heat and agitation with or without air. The oil contains certain substances which, when flocculated by the acid and temperature, fall down and mechanically (a term used in several recognized authoritative books) carry down other impurities. This process does not diminish the acid content of the oil so treated.

3. Heating up under carefully-regulated temperature conditions with fuller's earth, bone-black, etc., and filtering. This process also yields an acid oil.

4. Adding caustic alkalis, or alkaline earths, of an amount and strength determined by laboratory experience (Barreswil, beginning nineteenth century), heating to the "break," settling and drawing off the oil, which floats upon the soap stock or "foots." This was supposed to give a neutral oil, but not until it had been washed several times with water.

Yet as late as last year a distinguished oil chemist, in a very interesting summary of the "Contributions of the Chemist to the Cotton-seed Oil Industry,"¹ said "the chemist * * * found that the quality of the oil followed the free fatty acid present." An empirical formula has been worked out to show this relationship to the free fatty acid. The rule is: Multiply the f. f. a. by 2 and add 4; that is, an oil showing 2 per cent f. f. a. should give a shrinkage of 8 per cent. This is true only in a general way. I recently had a cotton-seed oil with 1.7 per cent f. f. a., which showed a shrinkage of 21 per cent by the official method of the Cotton-seed Crushers' Association.

The writer quoted above further said "the chemist's greatest service to the industry has been in the refining of the oil * * *."

Wesson was here referring more especially to edible cotton-seed oil. In that connection, Lewkowitsch, the lamented Anglo-German specialist in oil chemistry and technology, has said:² "No chemically-treated oil or fat can be looked upon as a product fit for human consumption." I confess inability to comprehend this sharp distinction as to what is meant by a "chemical." (Oxygen from a chromate is a chemical; oxygen of the air is not. Sulphuric acid is a chemical; caustic soda is not. It may be interjected here that certain statements transmitted by texts and sanctioned by law call for clarification and revision. No treatment of an oil or fat, which involves purification, rendering it palatable, agreeable to the sight, and avoids the introduction of constituents which may interfere with normal digestion should be forbidden. For fear of misunderstanding, it may be stated here that the method described below complies with all the most rigid laws of all nations and even the above-mentioned uneven discriminations.

An oil that is acid is unsatisfactory as a food. Acid oils corrode the vessels and generate objectionable

gaseous products when used as burning fluids. Acid oils corrode the bearings when used as lubricants; so it is desirable to have neutral oils for many purposes. Yet a neutral oil does not "cut" into white lead, for example, so an acid oil is preferred as a paint vehicle; but (Gardner has pointed out that the oil should not be too acid.

I have been more concerned with neutral oils and their production, so shall confine my remarks to preparation of that class of substances.

The present customary practice for refining vegetable oils referred to (the fourth mentioned above) depends upon neutralizing the free fatty acids in the crude oil usually by agitating the oil with an aqueous solution of an alkali, the strength and the amount having been previously determined by laboratory tests, agreed upon as a standard, and then heating the mixture during agitation to a suitable temperature until the oil "breaks." The mass is then allowed to stand until the "foots" settle to the bottom of the kettle, when the supernatant oil is drawn off by means of a swivel siphon. According to the process of Chisholm, sodium silicate is added to facilitate the settling. Invariably some "dreg" floats on top of the oil. If this be very great its settling is sometimes facilitated by throwing salt on top of the oil in the kettle. The salt drags down some of the floating "dreg." In any event, the oil drawn off is clouded, perhaps on account of the presence of some dissolved soap or globulated moisture or suspended matter—all doubtless colloidal in nature. This oil is then "brightened" after drawing off by throwing in small amounts of fuller's earth, heating again, and passing through a filter-press. Sometimes, previous to this treatment with fuller's earth, the decanted oil is heated to 160° to 180° F. in a settling tank to cause the "foots" remaining in the oil to rise to the top, when it is skimmed off.

The time factor in settling (six to twelve hours) of the "foots" materially affects the completeness of the separation referred to above. Coconut oil sometimes requires forty-eight hours to settle. In any event, the "foots" is wet with oil. The "foots" also entrains oil. Consequently during the rush season the efficiency of yield of refined oil must be sacrificed for speed and quantity refined. In other words, the more speed in refining, the more loss of refined oil, whatever the analysis, upon which purchase and sale are based, may indicate.

A process which would reduce the amount of oil entrained in the "foots" to a minimum, thus increasing the yield of refined oil, and one which would not be dependent upon the slow subsidence of the "foots" (that is, admit of rapid separation with consequent increase in capacity of a refinery), therefore, seemed to me not only to be desirable, but, if secured, would approximate the highest efficiency one might hope for in such an industrial operation.

I have succeeded in working out such a process, and shall now proceed to describe the principles involved

¹Journ. Ind. and Eng. Chem., 7 (1915), 277.

²Vol. 2, p. 32, 3rd edition. Vol. 181, No. 1056-53.

and at the same time demonstrate it to you as an analytical method. I have pleasure in exhibiting to you samples of the crude and refined (by my method) oils from a variety of sources.

The technical laboratory tests with batches of twelve to twenty pounds have been verified in the factory on a commercial scale. Some of the samples exhibited are from factory runs.

The aims to be accomplished are:

1. To reduce the amount of oil entrained in the "foots," thus increasing the yield of "whole oil."
2. To reduce the time of contact of the excess alkali (necessary for the "break" and to secure the best "color") to the minimum.
3. A technological corollary calls for the utilization of any by-products.

It is to be assumed that all oils, good, bad, and indifferent, are to be treated. However, this may not be necessary, as in some cases only the good, and perhaps the indifferent, oils are refined under the old practice at some places. Certain foreign markets call for a highly-colored oil, so they do not present the problem of bleaching.

In my investigations, lasting through several years, I have taken various kinds of crude vegetable oils from various kinds of sources with various (extreme) conditions and refined them. In many cases I have been told that no attempt would ordinarily be made to refine a particular oil, as it should be sent to the soap-kettle, the corresponding price only being expected. Such oils would have represented much better values if they could have been refined by the usual practice. These oils in every case have yielded to my process, have been refined, and with a saving over the old processes. I may say, however, that China wood (tung) oil, castor oil, and aged linseed oil cannot be economically refined by the process. I wish also to repeat that I am referring to the production of neutral refined oils only.

If we can get the "foots" into such a condition that it may be filtered and then squeezed, we may reduce the amount of "whole oil" entrained.

If we can do this immediately after the "break" and while the oil is still hot, we shall be able to reduce the time the "whole oil" is exposed to the saponifying action of the excess alkali necessary to secure proper color, avoid the present practice of necessary "cleaning," and the second heating.

I have called your attention to the presence of bodies, which in general terms are called colloids, in oils. These colloids may or may not be colored; may or may not make the oil turbid. I have also shown that some colloids may be and are coagulated by heat, some by acids, some by alkalies, some by salts or electrolytes, and in time will settle out. Colloids that have been coagulated or lumped may be filtered out. Some coagulated colloids in their formation absorb coloring matter. The problem of economical filtration on the large scale necessary was one of great diffi-

culty; in fact, so far as I am aware, it was unsolved previous to my investigation. Suitably-prepared cellulose fiber will absorb some coloring matter. It will bring about an agglomeration of the material precipitated from oils by treating the oil with alkalies and heating, and it will bind the particles together so that they may lose their somewhat slimy character and then may be easily filtered away from the oil in which they were produced. Short-fibered "linters" or "delint" is a suitable form of cellulose for some oils.

Therefore I add cellulose, suitably prepared, along with the caustic to the oil to be refined. The "break" takes place normally on heating as in the ordinary process, but the precipitated mass is in such a physical condition that it may be separated from the oil immediately by filtration.

As mentioned above, some colloids, perhaps colored, are thrown down by salts, so in certain cases some salt (1 per cent of sodium chloride) may be added. If there be a slight excess of water present, the sodium chloride serves also to "salt out" any soap in that water. The addition of salt, however, is not necessary in all cases.

I have also discovered that the tendency of the soaps formed by the caustic-alkali treatment to emulsify with the oil, or so to distribute themselves through the oil as to render their separation difficult, may be overcome by subjecting the oil, at a suitable stage of the treatment, to the action of an anhydrous salt which is capable of taking up water of crystallization, the preferred salt being dry sodium carbonate (soda ash), which, as is well known, is capable of taking up one, seven, or ten molecules of water of crystallization, according to temperature conditions. By such treatment the soaps which have already been formed by the treatment with caustic alkali, and which have become so incorporated with the oil as to be incapable of complete separation by ordinary filtration, are hardened or pectised, presumably by dehydration, and are so modified that they are readily separated by simple filtration. Sodium sulphate, which acts in the same way, may be used instead of soda ash.

The process is carried out by adding ordinarily 2 per cent of prepared cellulose (less than 1 per cent real cellulose) and a suitable amount of caustic soda (usually much stronger but actually less in amount than is commonly used). The whole is thoroughly basted by mechanical means and then heated to 45° to 65° C. to produce the "break"; a determined amount of soda ash is added, after which it is filtered. At first some soap may pass through the filter-cloths. In that event, the first filtered oil may be run directly back into the refining kettle and pumped through the press until the oil is "bright." This usually occurs within a few minutes; in fact, the speed of filtration is directly dependent upon the speed of the pumps. This re-filtration also improves the color. This oil is neutral and can be deodorized and bleached, or both

at once, or may be stored safely. If linters is used, $\frac{1}{4}$ to $\frac{1}{2}$ per cent of the dry cellulose is added.

These ideas are covered by four United States patents granted, Nos. 1,105,743, 1,105,744, 1,114,095, 1,130,008, and others applied for.

The danger of making a whole kettle into soap stock through failure of the refiner to be "on the job" is reduced to a minimum, as in several thousand trials this has not occurred, the trials being made by different people with various grades of oils of different

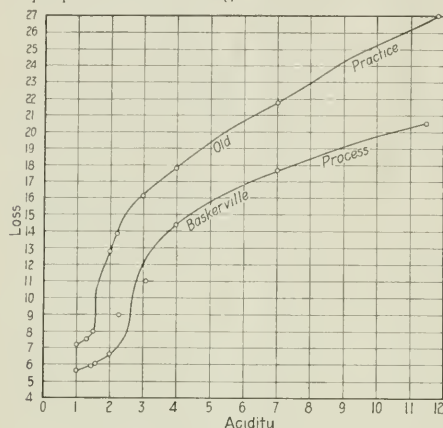


Fig. 1.

character. In other words, the process is near "fool-proof." Any man of fair intelligence can operate the process, and the air of mystery surrounding the professional refiner is dissipated. The superintendent has a double check on the refinery by weighing the finished oil and cake. The daily reports when summed up should coincide with the annual inventory. I have known of cases where as much as 100,000 pounds of oil have failed to appear in the annual inventory, but were reported daily and had to be charged up to profit and loss at the end of the fiscal year when the operation was under the usual process.

The following curves have been prepared from a series of cotton-seed oils very variable in character (Fig. 1). The second chart (Fig. 2) shows the comparative losses with several other oils. They show the comparative losses by the normal present practice and my process.

I have also been able to secure a further 1 to 3 per cent saving by subjecting the "cake" to hydraulic pressure. This extra saving is not shown in the charts.

The process is very rapid, the controlling factor being filter-press capacity. A study of plate filter-presses has indicated a preference for a center-feed press making $1\frac{1}{2}$ to 2-inch cakes. The filter-press problem in connection with the process is not one of filtering area, but cake capacity. Presses, as the Kelly or Sweetland, which are dumped mechanically, meet the conditions better than plate presses. A new

Sweetland press recently devised for this process promises the best results. It is provided with bottom exits for the refined oil, and the under bivalve swings through an arc of 105 degrees. Monel metal filter-cloth makes the machine practically permanent. By a slight increase in filter-press capacity the output of a refinery may be doubled or even tripled.

UTILIZATION OF BY-PRODUCT.

The cake may be converted directly into soap, the cellulose becoming very finely comminuted. It is partially mercerized, partly converted into a colloid, and some of it forms an unobjectionable filler for some grades of soap, especially soap powders.

The cake may be "cut" with acid directly. The cellulose settles quickly in the aqueous layer from the black grease, which latter may be drawn off ready for market or use. When the cake is to be "cut," in order to reduce the amount of acid necessary, I prefer to use salt cake in place of soda ash as the "agglomerator."

A solution of nitre cake, the process of Dr. Jeffrey Stewart, of Philadelphia, patent assigned to the du Pont de Nemours Company, for the recovery of oil from soap stock, can also be used in cutting the cake. In view of the high price of acid at present, this may

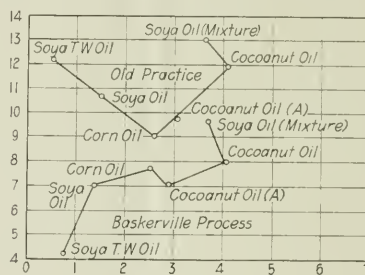


Fig. 2.

serve as an economical method for making "black grease."

Printed instructions for the use of the method in practice or as analytical procedure will be supplied to any who will write for them.

SUMMARY.

A process has been worked out, based on scientific principles, for preparing neutral oils, which possesses the following advantages:

1. The actual refined oil obtained is from 1 to 10 per cent more than now secured. Placed at a low average of 3 per cent, the process will save the cotton-seed oil industry in this country over \$2,000,000 a year when prices are normal. The soja-bean oil industry, just developing in this country, can save 5 per cent. The peanut oil industry can save 6 per cent. The coconut oil industry can save from 3 to 5 per cent.

2. The process takes from one-tenth to one-third the time now necessary. Hence the capacity of the refinery is increased. This is of great importance dur-

ing the rush season; in fact, its introduction will in economic efficiency perform the same role the tungsten filament lamp has played in the electric lighting industry, whereby the light production of a power station has been tripled.

3. The process gives a daily double check on the efficiency of the refinery.

4. The process is applicable to all grades of edible oils, which is not true with the common procedure.

5. Little new machinery is needed. The extra filter-press capacity called for will be more than paid for in the first year's profit.

6. The cost of chemicals is the same or less.

7. The by-product cake may be converted directly into a useful and commercial material.

Bauxite and Aluminum Industries.

The bauxite and aluminum industries in the United States had a banner year in 1915. The production of bauxite was 297,041 long tons, valued at \$1,514,834, an increase of 77.723 long tons, or 35 per cent in quantity, and of \$445,640, or 41 per cent in value compared with 1914, according to a statement issued by the United States Geological Survey. This abnormally large increase in bauxite production is due to the greatly increased activity in the aluminum industry. The quantity of foreign bauxite used during the year was exceedingly small, for obvious reasons, and out of a total consumption of more than 300,000 tons only slightly more than 1 per cent was imported. Arkansas produced more than 90 per cent of the domestic production and Georgia, Alabama, and Tennessee contributed the remainder.

In spite of the fact that the metallic aluminum consumed in the United States in 1915 amounted to 99,806,000 pounds, there was a great scarcity of the metal in this country, especially during the latter part of the year, according to information gathered by W. C. Phalen, of the Geological Survey. A greatly increased demand, together with the curtailment of imports, were the chief causes of this scarcity.

The applications of the metal have been many in the war in Europe. Light aluminum alloys have been largely employed, and the metal itself has found favor in camp equipment and especially in the manufacture of automobile bodies and air craft of all kinds. Aluminum powder has been extensively used in making ammonal, a high explosive, by mixing it with ammonium nitrate. The explosive is reported to be insensitive, very stable, and destructive.

The Geological Survey now has available for distribution its annual statement on gold, silver, copper, lead, and zinc in the eastern states in 1915. The total value of the output of these five metals for the year is given as \$29,968,372, an increase of nearly 158 per cent over the production in 1915.

THE NEED OF CO-OPERATION BETWEEN MANUFACTURERS AND BANKERS.*

By F. C. SCHWEDTMAN.†

The year 1916 should be marked by a special effort toward organized co-operation between enlightened manufacturers and enlightened bankers of the United States. Whether it be in home or in foreign commerce, there is a particular need for these two classes to organize their activities in close co-operation with each other; for the interests of the two—business, humane, and patriotic—are in common to a very large extent. Both at home and abroad there have arisen many new problems which offer us new opportunities and which lay upon us new duties. These are not of our own making; they were made for us, and we owe it as a duty to ourselves and to the world at large to show that we are equal to them.

For some of our enlightened manufacturers the day is past when competition necessarily means antagonism. They have learned to meet and to co-operate with competing manufacturers, as well as with jobbers, dealers, and consumers, to the benefit of all. There does not exist, however, sufficient systematic co-operation between American manufacturers and bankers, and in this respect we differ greatly from European nations which have built their success in home and export industries primarily upon a close sympathetic bond between these two interests.

From my experience of many years with manufacturers I know that some do not look upon banks as their friends, but that in many cases they regard them rather as their antagonists or oppressors. On the other hand, bankers not infrequently look at loans to manufacturers with more than ordinary care and often with suspicion. Let me give you an illustration of the former attitude. A short time ago I received a letter from a manufacturer in the middle west—the active head of a corporation established by his father forty years ago, and doing now nearly a million dollars' worth of business a year. The concern has an enviable reputation in every direction. From this letter I quote:

As you probably know, we have kept our noses to the grindstone, saved and scrambled and got along the best we could with very little assistance from the banks, because of my father's inborn fear that when you go to a bank you are already knocking at the doors of the bankruptcy court.

What brings about this unnatural condition? Is it the fault of the banker? Is it the fault of the manufacturer? I believe that lack of understanding of each other's problem is at the bottom of it. Might not a free and open exchange of views bring about a more helpful and healthful condition for both sides, as well as for the industries and the people of the United States?

If the banker does not understand the soundness

*From an address delivered July 12 at the Convention of the National Fertilizer Association.

†National City Bank of New York.

of a manufacturer's financial statement, he should be, and I believe would be, glad to be convinced of the correctness of the manufacturer's view-point. If, on the other hand, the manufacturer does not realize that he is pushing his bank credit too far for his own safety, or that there is something about his operations or his statement which does not seem sound and conservative, I am sure the manufacturer should be, and usually would be, anxious to be set right by the banker. Both have everything to gain and nothing to lose by a more intimate knowledge of each other's problems and difficulties.

Let us grant that there are still bankers with reactionary tendencies just as there are manufacturers of the same type; there is that much more reason for the enlightened members of the two fraternities to get together and to establish a preferred class along the lines of preferred risks in fire insurance. We all know that in ordinary fire insurance the cost is comparatively high, because no matter how careful we may be we must pay part of our careless neighbor's losses. We know also that a concern willing to use fireproof construction, and to equip its property with sprinklers and with the most improved safety devices, can buy insurance at one-tenth the cost of average rates, in insurance concerns making high-grade risks a specialty. The low-grade risk will not be taken by such an insurance company at any price.

Surely the best manufacturing concerns and the best banks can co-operate by establishing a high-grade fraternity to which only the best are admitted—a brotherhood which will reflect credit upon everyone connected with it, and which will serve as a model for the highest development of efficiency in modern manufacturing and banking.

It is difficult for some of my manufacturing friends to think of banking as requiring initiative, courage, and ingenuity; and yet there is no line of activity which requires more of those and many other qualities than does modern banking. Let me tell you a little story, pointing its own moral.

An old, established English banking house had a branch house manager in Central America. The regular shipment of cash was on the way, and ordinarily would have been in ample time for all business requirements, but the boat was delayed. The manager kept cable and wireless busy, but meanwhile the cash in the bank was running short. Finally, he had assurance that cash would reach him in two days; but what could he do in the meanwhile to save the reputation of his institution and to retain the confidence of the public. To be short of cash even for a single payment might mean a run, which would undo years of patient, hard up-building. If only one of the many feast days would fall upon the morrow all would be safe. Then a thought occurred to him. In the morning there was a sign upon the bank door, which read: "Closed for today on account of an English feast-day." The day after, the cash shipment was in, everything

was all right, and everybody was happy. The ingenuity of a young banker had saved the day.

Too many people still look upon a bank as merely "a place to put money for safe-keeping." A good bank performs a much more important function; it brings together small amounts of capital so that they may be employed in profitable enterprises. Hoarded capital is a menace. Deposited with a good bank it works for the owner and plays an important part in the prosperity of the community. Safety, uniformity, and elasticity, are the three props upon which a successful currency system must rest; and these qualities every good bank possesses. Safety was gradually acquired by the state-owned banks of the middle of the nineteenth century; uniformity, by the national banks of the latter part of that century; and elasticity, by the Federal Reserve System. The Federal Reserve Act, however, has done more than to provide elasticity; it has made it possible for national banks to establish branches in foreign countries.

You are probably aware of the fact that the National City Bank, with which I have the honor to be connected, is the first, and so far the only American financial institution which has gone into foreign branch banking upon a comprehensive basis. This is of vital interest to the manufacturer, because branch banks are important factors in buying from foreign nations and in selling to them raw stuffs and manufactured articles.

The European war has made necessary many a shift and change in foreign banking and in foreign trade relations. Many of the nations which cannot, or will not, carry on international commerce directly with each other must use indirect routes, and large American banks with international reputations are, naturally, often the agencies. The National City Bank has had to establish a number of special departments to care for the need of its manufacturing and other customers. We have, among others, a mercantile department, where we have handled rugs, tobacco, and opium from Turkey; chemicals and mushrooms from Russia; tea and raw silk from China; figs and bay-leaves from Greece; cocaine, wool, and silver ore from Peru; coffee from Colombia; and rubber from Sumatra. We have direct representatives in almost all parts of the world, and you gentlemen know that there is no better way of building up, on a permanent basis, satisfactory business either at home or abroad than by direct representation. It is difficult for the ordinary manufacturer to do business always directly, even at home, but it becomes impossible abroad. It is for this reason that we have attached commercial representatives to each of our six South American branch banks. These men are experts; they gather first-hand information as to what is wanted in the way of merchandise and manufactured articles. By means of letters and publications their reports are widely distributed among American manufacturers. Special reports can also be secured through these representatives when

needed. This service is widely used and is much appreciated by large numbers of American business houses, and, yet, it seems to me, the manufacturers of the United States are by no means making the best use of their opportunities either at home or abroad.

It is a sad reflection upon American business men that only about one out of four succeeds. If the ordinary business man does not know his costs or his profits—it is my experience that six out of ten do not—how can the banker know which account is sound and which account is not? This uncertainty is responsible for much suspicion and mistrust. It must be overcome by active co-operation.

It is surprising how many questions, large and small, can be solved by closer contact between banker and manufacturer. Only a short time ago an official of the foreign department of a large bank told me that two large manufacturing concerns handled their export documents in entirely different ways; one, by co-operation with the bank, enabled the department to handle twelve in the time required to handle three of the concern unwilling to co-operate. Both concerns handle dozens of export shipments daily. Needless to say, the shipments of the co-operating concern automatically receive better and quicker attention.

Take, again, the question of cost. If manufacturers generally realized how much importance a thoughtful banker places upon a good cost system, there would be less hard feelings. James Bryce, the celebrated Englishman, says: "Three-fourths of the mistakes that a man makes are made because he does not really know the things he thinks he knows." Under ordinary conditions, failure will come to any concern that does not know its costs. Manufacturers and bankers might well develop in co-operation a standard form of cost system, which would assure both efficiency and simplicity. Your organization can be of untold assistance to all your members by gathering and standardizing cost and credit information. It would be an effective and perfectly legal means of reducing unfair competition. I am told that in connection with foreign trade a number of manufacturers might combine, and pool their interests in such a way as to reduce the selling and distributing cost without violating anti-trust laws.

Again, much educational effort might be carried on among manufacturers to impress upon them the great importance of keeping their resources as far as possible in liquid form. From personal investigation I know of more manufacturers getting into financial trouble by tying up money in expensive building than by any other one thing. In all these directions progressive bankers will gladly co-operate with manufacturers. In fact banks can, and will do more; they can establish departments with special facilities for looking after the wants of manufacturers. A modern bank, with all its activities, becomes necessarily a complex mechanism. There is a man for every transaction, but it is difficult for the uninitiated to find the right

man or the right department without loss of time and patience. If, however, the manufacturer can come to a special department, where his problems are understood, and from which he is taken at once to the right man, it means greater efficiency, more satisfaction, better business all around.

Many people associate a bank officer with big things and hesitate to talk with him about their seemingly unimportant problems. No one's business or financial problems are too small for the careful consideration of an efficient bank. Just as the modern manufacturer must specialize, so the modern banker must be educated to deal with special problems. It is for this reason that the National City Bank has in its new business department a special place for manufacturers, so that it may serve manufacturers with better understanding and higher efficiency. Not that I would for one moment recommend a single manufacturer to break home ties and to do business in New York in preference to doing it with his local banks. Your first and most important allegiance is to your home institutions. It is not, however, your whole duty. If national institutions can render you aid, which, owing to natural limitations, local institutions cannot render you, then it is good business and good policy to avail yourselves directly or indirectly of all the assistance you can secure.

Past and present efforts are only the path-finders of future co-operation. If American finance and American industry will but fully realize and grasp their opportunity, the future will be limitless in co-operative possibilities.

The broad field for future co-operation among manufacturers and bankers must be primarily along two lines—better control of our home markets and gain in foreign markets. In the past, many of the largest enterprises in the United States have been financed by European capital, and much of the capital stock in many of our great industrial institutions has been furnished and controlled abroad. Hereafter the American public must furnish this capital, and for that end American bankers must be the principal agencies.

American manufacturers must be largely responsible, too, for the efficient use of funds. It is the duty both of American bankers and of American manufacturers to see to it that investments are safe, and worthy of the full confidence of American investors. It is not enough, however, to strive for honesty, integrity, and efficiency in American industrial investments and management. Success is impossible without sound national policies in tariff legislation, in merchant marine, and in railway transportation requirements. An equitable protective tariff, providing for the difference between the labor cost here and that abroad, is required to keep American workmen employed at our established higher standards, while American built and operated ships are needed to keep the demand for American labor and material at a high point. Bankers and manufacturers can, and should, organize sys-

tematic co-operation to bring about a better public understanding of these fundamental requirements for a good home market.

The necessary co-operation for gaining larger foreign markets can best be illustrated by the recent organization of the American International Corporation—a fifty million dollar institution, closely associated with the National City Bank of New York. Mr. Frank A. Vanderlip is the chairman of the board of directors, and Mr. Charles A. Stone is the president of the company. The board of directors is composed of the best known leaders in American finance, in industry, and in transportation. Foreign commerce promotion is the chartered purpose of this great institution. How is this to be brought about? By selling to foreign nations, such as South America, China, Russia? How can they buy when they have not the money with which to pay? No, the campaign must be much broader. We must furnish a large part of the money required to develop their resources, but we must see to it that the supplies of raw and of manufactured materials required for American-financed foreign enterprises are furnished by American mines, mills, and farms. We must plan in such a way that American labor may receive the wages due for supplying the materials and the machinery for the foreign enterprises financed with American money.

Surely this is a suitable field for active co-operation between manufacturers and bankers. Wherever we turn, in whatever we do, we see standing clearly before us the need of organized co-operation between these two inseparable interests. The more frequently they meet, the more closely they become acquainted with each other, the better will they understand each other's problems. From this closer acquaintance, from this more complete understanding, will certainly follow more efficient co-operation.

Second National Exposition of Chemical Industries.

A great deal of interest is being manifested in the Second National Exposition of Chemical Industries which is to be held at the Grand Central Palace, New York City, during the week beginning Sept. 25. The exhibitors that have signified their intention of being represented already are more than twice the number that were at exposition last year. Much new apparatus and many processes will be exhibited for the first time. A motion picture program broader in scope than the one last year has been arranged for the coming exposition. Among the films already secured from large industrial corporations are the following: The match industry; mining and manufacturing of iron; the rubber industry; manufacture of explosives; varnish manufacture; making of blotting paper; silver mining; accident and fire prevention; manufacture and use of fertilizers; manufacture of steel; Spring meeting of American Society at Danville.

PURIFICATION OF WASTES FROM THE FINISHING OF WOOLEN GOODS.

By H. R. CROHURST* and A. D. WESTON.†

Experiments on the treatment of the wastes from woolen mills were made by the Massachusetts State Department of Health under the supervision of H. W. Clark, chemist, and the results published in their annual reports. Following is an outline of their work and the results obtained:

Experiments were made on the wastes from a mill in which woolen cloth was washed, dyed and afterwards washed again. Two small experimental filters were operated on this waste. Each filter was constructed of 3 ft. of sand having an effective size of 0.28 m.m. One filter was operated at a rate of 100,000 gallons per acre per day for two months with the raw waste and then for two months more at a rate of 55,000 gallons per acre per day with the supernatant liquor after chemical precipitation.

The use of 3,500 lbs. of lime per 1,000,000 gallons of waste caused a removal of 80 per cent of the nitrogen determined as albuminoid ammonia, over 90 per cent of the matters determined by oxygen consumed together with about 70 per cent of the organic matter determined by loss on ignition. As the waste amounted to 200,000 gallons per day, chemical precipitation would have cost \$2.00 per day.

A second filter was operated for four months with the waste, after sedimentation, without chemical treatment, at a rate of 100,000 gallons per acre daily. The effluent of both filters was always clear and non-putrescible, but sedimentation alone seemed to give as good results as chemical precipitation.

The character of the wastes and the results of the operation of these filters are shown in Table I.

The wastes from a second mill, consisting of the liquors from wool scouring, spent dye liquors, wash waters and wash waters from a shoddy mill were experimented with.

Three filters, one a trickling filter 6 feet in depth, of broken stone; the other two sand filters, 3½ feet and 2 feet in depth, of sand, having an effective size of 0.26 m.m., were operated with the waste. The effluent of the trickling filter was very little different than the applied liquor. The 2-foot sand filter was operated for three weeks at a rate of 1,500,000 gallons per acre per day until it clogged. Three inches of sand were removed from the surface and the rate reduced to 1,000,000 gallons per acre per day, but it again clogged. The clogging was due to the fatty matters present in the scouring liquor. This serves to bring out strongly the necessity of the separation of the wastes containing the grease and its treatment for recovery. The 3-foot sand filter was operated at a rate of 50,000 gallons per acre per day and then at a rate of 150,000 gallons per acre daily, with the

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effluent of the 2-foot sand filter. This effluent was always clear and odorless, but was somewhat colored by the spent dyes in it.

The results of the analyses of the applied liquor and the filter effluents follow in Table 11.

These results seemed to indicate that these wastes could be purified without any great difficulty by sand filtration at rates up to 500,000 gallons per acre per day. Sedimentation in ample settling basins should precede filtration. The wastes from the wool scouring processes should have a separate treatment before being added to the other wastes.

The wastes from a third mill consisting of the wash waters from washing, boiling and dyeing heavy woolen cloth were experimented upon. The wastes consisted of about one part spent dye and thirteen parts wash waters.

Two filters were operated with this waste. Number 1 was 3 feet in depth of sand having an effective size of 0.28 m.m. and was operated at a rate of 100,000 gallons per acre daily with the supernatant liquor from the waste after treatment with 5,000 lbs. of lime and 5,000 lbs. of copperas per 1,000,000 gallons. After a few weeks' operation the rate was cut to 50,000 gallons per acre daily. Filter No. 2 was 4 feet

deep and consisted of sand having an effective size of 0.25 m.m. The supernatant liquor after sedimentation only was applied to this filter. The rate at first was 100,000 gallons per acre daily, but later was changed to 50,000 gallons per acre daily. The effluent was always clearer than the effluent of No. 1 and was always non-putrescible. The experiments indicated that this class of waste could be purified by sedimentation and filtration through 3 or 4 feet of sand at rates not to exceed 50,000 gallons per acre per day. The results of these experiments are given in Table III.

TABLE III.—RESULTS OF EXPERIMENTS ON THE WASTES FROM WOOLEN MILLS.
Parts per Million.
FILTER NO. ONE.

Source.	Ammonia, Nitrogen as		Total residue.		Total loss on ignition.		Free.		Albuminoid.		Nitrates.		Nitrites.		Oxygen consumed.	
Raw waste	2,704	1,215	3.9	21.9	...	...	...	...	...	...	...	...	...	...	181.3	...
Applied waste	2,348	669	4.2	6.7	...	...	...	...	...	...	...	...	...	...	111.3	...
Effluent	1,768	32	.35	1.5	1.0	.03	...	...	...	...	...	...	...	...	19.3	...
Per cent removed.....	67	78	...	...	...	...	...	...	...	...	...	...	...	...	83	...
FILTER NO. TWO.																
Raw waste	2,704	1,215	3.9	21.9	...	...	...	...	...	...	...	...	...	...	181.3	...
Applied waste	2,645	1,111	3.9	9.5	...	...	...	...	...	...	...	...	...	...	142.0	...
Effluent	1,476	175	.1	8.0	.001	15.0	...	...	...	...	...	...	...	...	...	...
Per cent removed.....	84	92	...	...	...	...	...	...	...	...	...	...	...	...	89	...

The wastes experimented upon at a fourth mill consisted of the wash waters from the washing and dyeing of cloth and dyeing of raw cotton. In cloth washing the goods were first saturated with a soap solution in the fulling machines and then washed for half an hour. The dyes used were heavy logwood and aniline dye.

A mixture of the worst wastes from the mill were applied to a sand filter 3 ft. in depth, the sand having an effective size of 0.25 m.m. at a rate of 100,000 gal. per acre per day. The waste was turbid, pinkish, non-putrescible and deposited but a small amount of matter on standing. The filter removed 85 per cent of the organic matter, as indicated by albuminoid ammonia, and 89 per cent, as indicated by oxygen consumed. The effluent was always clear, colorless and non-putrescible.

The results of the operation of this filter are given in Table IV.

TABLE IV.—PARTS PER MILLION.
Ammonia, Nitrogen as

Source.	Ammonia, Nitrogen as		Total residue.		Total loss on ignition.		Free.		Albuminoid.		Nitrates.		Nitrites.		Oxygen consumed.	
Raw waste	1,623	624	1.0	5.8	...	...	...	...	...	...	...	...	...	...	114	...
Applied waste	1,506	516	.7	3.1	...	...	...	...	...	...	...	...	...	...	8.5	...
Effluent	1,153	126	.3	.5	.1	.02	...	...	...	...	...	...	...	...	1.0	...
Per cent removed—	7	12	30	42	...	...	...	...	...	...	...	...	...	...	22	...
Sedimentation	23	77	60	85	...	...	...	...	...	...	...	...	...	...	89	...
Filtration	29	80	72	91	...	...	...	...	...	...	...	...	...	...	91	...
Sed. and filtration.....	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...

TABLE I.—FILTER OPERATING ON CHEMICALLY PRECIPITATED WASTES.
Parts per Million.

Source.	Total residue.		Total loss on ignition.		Free.		Albuminoid.		Nitrates.		Nitrites.		Oxygen consumed.	
Raw waste.....	1,187	476	1.2	8.9	...	...	...	...	...	...	...	...	199	...
Applied waste.....	1,664	131	0.7	1.3	...	...	...	...	...	...	...	...	29	...
Effluent	1,218	87	0.5	0.95	0.7	.06	...	...	...	...	...	...	16	...
Per cent removal—	...	...	...	...	...	...	...	...	...	...	...	...	...	...
By precipitation.....	...	72	38	85	...	...	...	...	...	...	...	...	85	...
By filtration	27	34	31	29	...	...	...	...	...	...	...	...	46	...
Precip. and filtration.....	...	82	57	89	...	...	...	...	...	...	...	...	92	...
Filter Operating on Settled Waste.														
Raw waste	1,187	476	1.2	8.9	...	...	...	...	...	...	...	...	199	...
Applied waste	1,239	285	1.0	3.0	...	...	...	...	...	...	...	...	119	...
Effluent	1,053	104	0.2	0.7	0.0	...	...	...	...	...	...	...	24	...
Per cent removal—	...	...	...	...	...	...	...	...	...	...	...	...	...	...
By sedimentation	...	40	16	67	...	...	...	...	...	...	...	...	40	...
By filtration	15	64	79	75	...	...	...	...	...	...	...	...	80	...
Sedimentation and filt. ..	11	78	82	92	...	...	...	...	...	...	...	...	88	...

TABLE II.—RESULTS OF EXPERIMENTS WITH WOOLEN MILL WASTES.
Parts per Million.

Unfiltered—	Raw waste.	Settled waste.
Total solids	1,500	941
Loss on ignition.....	600	269
Fixed solids	900	672
Filtered—	1,080	...
Total solids	...	...
Loss on ignition	302	...
Fixed solids	778	...
Ammonia—	...	...
Free	5.8	4.8
Albuminoid total	8.0	3.1
Albuminoid suspended	3.0	...
Oxygen consumed	81.4	36.1

ANALYSES OF SAND FILTER EFFLUENTS.

	Two-foot sand filter.	Three-foot sand filter.
Free ammonia	2.347	3.839
Albuminoid ammonia	1.614	.703
Nitrates	.3	3.7
Nitrites	.004	.092
Oxygen consumed	18.8	12.9

moving 50 per cent of the total organic matter and filtration removing 75 per cent of that remaining.

Shoddy Mill Wastes.—In 1906 the Massachusetts State Department of Health made experiments upon the wastes from a shoddy mill, consisting of the water from the washing of rags after carbonizing and the spent dye liquors from dyeing. The wastes from dyeing were very small. The wash waters from the carbonizing process contained considerable acid, 250 to 1,200 lbs. of lime per 1,000,000 gal. of waste being required to neutralize it.

This waste after neutralization was applied for two months at the rate of 100,000 gal. per acre per day to a filter 3 ft. in depth, the sand having an effective size of 0.28 m.m. The effluent was always clear, colorless, non-putrescible and nitrification in the filter was active. The average analyses of the raw waste and the filter are given in Table VII.

TABLE VII.—PARTS PER MILLION.
Ammonia, Nitrogen as

Source.	Total residue.	Total loss on ignition.	Free.	Albuminoid.	Nitrates.	Nitrites.	Oxygen consumed.
Raw waste	717	369	6.4	4.3	..	..	44
Applied waste	536	101	6.2	1.3	..	..	19
Effluent	611	94	0.2	0.5	10	0.4	7
Per cent removal—							
Sedimentation	25	73	3	70	..	..	56
Filtration	15	97	59	..	..	..	65
Sed. and filtration	15	75	97	88	..	..	85

Further experiments were made upon this class of wastes in 1908. The waste before being applied to the filter was first settled and a small amount of suspended matter settled out. The liquid was then filtered through sand, first at a rate of 100,000 gal. per acre per day, and later at a rate of 150,000 gal. per acre daily. The effluent was always satisfactory and well nitrified. Table VIII shows the results of sedimentation and filtration.

TABLE VIII.—FILTRATION OF SHODDY MILL WASTES.
Parts per Million.

Source.	Ammonia Free.	Albuminoid.	Nitrogen as Nitrates.	Oxygen consumed.	Hardness.
Raw waste....	9.5	4.1	..	31	..
Applied waste.	8.0	1.3	..	10	130
Effluent	0.8	0.6	12.8	0.2	8 15

The Filtration of Dye Liquors.—The treatment of highly colored dye liquors has been studied at the Massachusetts State Department of Health's experiment station at Lawrence, Mass., along with other trade waste problems.

Chemical treatment of the wastes by precipitation with lime, ferric chloride, copperas, iron, alum, etc., was studied. The best results were obtained with lime and ferric chloride in various proportions, the greatest amount never being over one ton per 1,000,000 gal., which amount often removed practically all of the coloring matters.

The supernatant liquor after chemical treatment was applied to two sand filters. One sand filter, 4 ft. in

depth, with sand having an effective size of 0.27 m.m., was operated at a rate of 2,000,000 gal. per acre per day and gave the following average analyses for six months:

Parts per Million

Color	Pale yellow
Free ammonia	3.73
Albuminoid ammonia	0.93
Nitrates	1.20
Oxygen consumed	15.4

A filter of soft coal ashes 4 ft. deep, operated at a rate of 2,000,000 gal. per acre per day, gave the following average analyses:

Parts per Million.

Color	Light yellow
Free ammonia	5.00
Albuminoid ammonia	1.05
Nitrates	0.30
Oxygen consumed	13.5

The sludge produced by the chemical treatment of the dye liquors with precipitants was treated on a filter 2 ft. in depth, composed of soft coal ashes, at a rate of 40,000 gal. per acre daily. The dose usually disappeared in 24 hours, but during the five months it was in operation it was necessary to remove the sludge from the surface four times. The effluent was clear and colorless and contained only a small amount of the organic matter, as shown by the following average analyses:

Parts per Million.

Turbidity	None
Color	0.5
Free ammonia	3.52
Albuminoid ammonia	0.10
Nitrates	1.70
Nitrites	0.01
Oxygen consumed	1.00

Three other filters were operated with the waste dye liquor from one of the mills at Lawrence. Filter number 1 was a sand filter 5 ft. deep and was operated at a rate of 50,000 gal. per acre per day for seven months and produced a clear effluent having a pale yellow color and removed 95 per cent of the organic matter. Filter number 2, a coke contact filter, operated at a rate of 400,000 gal. per acre daily for three months, removed less color and 80 per cent of the organic matter. Filter number 3, a trickling filter of broken stone, operated at a rate of 540,000 gal. per acre daily, removed still less color and 70 per cent of the organic matter. Following, in Table IX and X, are the averages of the applied liquor and the effluents of these three filters.

TABLE IX.—FILTRATION OF DYE LIQUORS.
Parts per Million.

Source.	Ammonia Free.	Albuminoid.	Nitrogen as Nitrates.	Oxygen consumed.
Dye liquor	Decid.	Strong	3.28	2.62 0.0 63
Sand filter effluent	None	None	0.22	0.19 2.9 4
Contact filter eff.	V. Sl.	V. Sl.	2.41	0.67 0.4 11
Trickling filt. eff.	V. Sl.	Sl.	2.61	1.03 0.9 19

TABLE X.—AVERAGE PERCENTAGE REMOVAL OF ORGANIC MATTER FROM DYE LIQUOR BY VARIOUS TREATMENTS.

Chemical treatment—	Per cent removed—	Albuminoid ammonia consumed.
Two hours' sedimentation	21.3	75.0
Sixteen hours' sedimentation	46.0	64.0
Effluent of sand filter after chemical treatment	78.0	88.0
Effluent of sand filter without chemical treatment	94.0	96.0

Stabler and Pratt, in their investigations of the disposal of wastes from textile industries, made experiments upon the filtration of dye liquors from the R. D. Mason Company's plant at Pawtucket, R. I. The dye liquors treated here were from the dyeing of cotton yarn. While the operations and the colors used in dyeing various classes of goods may differ, the waste liquors from all dyeing operations are more or less similar. This waste varies considerably, even through the day, because of the many and different processes being carried out in the dye house, and consists of relatively small amounts of spent dye in large volumes of water. Table XI shows an average and the maximum and minimum determinations of the waters experimented on at Pawtucket.

TABLE XI.—ANALYSES OF THE LIQUOR FROM THE DYE DRAIN OF THE R. D. MASON COMPANY, PAWTUCKET, R. I.
Milligrams per Liter.

	Average analysis.	Maximum determination.	Minimum determination.
Solids—			
Total	1,470	1,576	570
Dissolved		1,482	612
Loss on ignition—			
Total	450	764	306
Dissolved		340	168
Free ammonia	1.8	4.9	0.3
Organic nitrogen	5.2	15.5	1.0
Oxygen consumed	240	660	85

Analyses by G. H. Pratt.

The dye liquors as represented above were treated on sand filters. Two beds, with a depth of $3\frac{1}{2}$ to 4 ft. of sand, having an effective size of 0.24 m.m. and a uniformity coefficient 3.4, were operated with this waste. Filter number 1 was first operated at a rate of 100,000 gal. per acre per day, during which time it gave an effluent of good appearance free from color and low in organic content. After a little less than two months' operation the rate was changed to 400,000 gal. per acre daily, and after about six weeks' operation the rate was again reduced to 100,000 gal. During the latter operation the effluent showed color and the analyses were unsatisfactory, the high rate of filtration, combined with extreme cold weather, causing the deterioration.

Filter number 2 was operated at a rate of 200,000 gal. per acre daily throughout the experiments. The same deterioration of the effluent was noticeable during cold weather. The effluent contained nitrites, but nitrates were never high, although present at times.

The organic purification of dye liquors by filtration are given in Table XII.

From these experiments it appeared that about 95

TABLE XII.

	Per					
	Milligrams per liter.			cent removal.		
	Free ammonia.	Organic nitrogen.	Oxygen consumed.	Free ammonia.	Organic nitrogen.	Oxygen consumed.
Waste from drain.....	1.8	5.21	240	..	..	..
Av. of 5 analyses, effluent filter No. 1, rate 100,000 gal.	.81	.37	6.4	55	93	97
Av. of 5 analyses, effluent filter No. 2, rate 200,000 gal.	.89	.67	11.8	51	87	95

per cent of the organic matter and nearly all of the color of spent dye liquors could be removed by sand filtration at rates not to exceed 100,000 gal. per acre per day.

Partly because of the limited sites available and partly to obtain a partial purification of waste dye liquors and wash waters which with the addition of fresh water could be used again in the mills, numerous patented apparatus have been devised along the lines of water purification principles, and many of these have been installed, more particularly at English mills. Among these may be mentioned Waite's apparatus, Mackey's apparatus, Watson's plant, Archbutt-Deeley system, and Bell's apparatus. The purification of the trade wastes in all of these depends upon chemical precipitation, followed by sedimentation, or sedimentation and straining through filters of various materials. The precipitants used are lime, aluminiferous, aluminum sulphate and soda, or combinations of the above. The first two systems depend upon sedimentation in cylindrical settling tanks, the upward velocity being reduced so that the precipitated sludge collects in the bottom of the tank, from which it is discharged onto sludge drying beds. The next two systems have rectangular settling tanks and sludge drying beds. Bells' apparatus is designed as a rapid sand filter plant and consists of a cylindrical settling tank and filter of the rapid type, provided with wash water devices, a strainer system, stirring apparatus, etc.

The actual purification obtained by these plants other than the removal of suspended solids is not very high, and probably not as great as could be obtained by chemical treatment and sedimentation in ample settling basins of the ordinary type. The removal of the suspended matter and partial purification does, however, make the wastes available for reuse and they are so used at several plants, being a source of profit both from the saving on the cost of water and by its conservation in times of drought when shutting down the plant might be necessary.

A study of the experiments on the treatment of this class of waste liquors indicates that the wastes from the finishing of woolen goods can be treated by sewage methods; that is, by sedimentation and filtration, or straining, provided those wastes which contain grease and which clog filters of this kind are treated separately. Excluding this latter class of waste, the wash waters and the waters containing the spent dyes can be purified by sedimentation, followed by filtration through sand at a rate not to exceed 100,000 gal. per acre per day. At this rate 78 to 92 per cent of the organic matter determined by albuminoid ammonia, 83 to 89 per cent as determined by oxygen consumed and about 80 per cent of the organic and other matters determined by loss on ignition can be removed from the waste.

Shoddy wastes neutralized, settled and treated by filtration, can be purified at a rate of 100,000 gal. per acre per day.

For the dye liquors alone the rate of 100,000 gal. per acre daily on sand filters will remove nearly all of the color and about 95 per cent of the organic matter.

Where the mill discharges wastes from the washing of woolen cloth, containing considerable grease, it is recommended, as already stated, that this be separated from the other wastes and be treated for the recovery of the grease and the acid waters resulting, after neutralization, be treated with the wash waters by filtration. The method proposed for the recovery of grease, as already described in another article, is the cracking process. By the recovery of this grease the return will be at least enough to pay for the operation of this portion of the works and will remove from the wastes the grease, which interferes with sewage methods.

The sale of grease from a plant at Pittsfield, Mass., already described, where the wastes from scouring were treated, showed a slight profit over the operating expenses, and a similar plant at Barre, Mass., was doing about the same.

The following two cases are taken from Wilson and Calvert in Trade Waste Waters and show the cost of operating such plants and the return from the grease recovered at English mills where woolen goods are finished. It is realized that English conditions are very different from those in this country and that the profits obtained there cannot be realized here, but the costs of operation will give some idea of what might be expected.

At the first mill heavy woolen goods were manufactured. During a year's operation 4,000 pieces were made, each 80 yards in length; 1,000 gals. of water were used per piece. The goods weighed 30 to 40 ozs. per yard. The oil used in the manufacture amounted to 59.5 tons, which was recovered in the plant and reused with 16.8 tons purchased. The soap used cost \$67 and amounted to 1,568 lbs., of which 784 lbs. may be reckoned as oil, making a total of 76.6 tons of oil in the waste. Forty tons of soda ash were used in the scouring, cost \$897.34. The piece scouring wastes were treated at this plant by first being passed through a screening apparatus to recover flocks and then pumped to the recovery plant, treated with acid to separate the grease and the acid liquor neutralized and strained through a cinder filter.

Operating expenses—	
Lime per year.....	\$ 5.35
Labor (one man at \$7.30 per week).....	389.32
Acid	206.34
Steam and water for presses.....	243.33
Cloth for magma.....	7.54
Total	\$ 851.88
Returns—	
Oil recovered	\$2,607.22
Flocks recovered	40.15
49 tons pressed cake.....	109.01
Total	\$2,756.38
Profit and loss account—	
Interest and depreciation, 10 per cent on \$2,740.....	\$ 274.00
Operating costs	851.88
Total	\$1,125.88
Annual profit	1,630.50

A second mill extracts the grease from the thicker suds from scouring fancy woolen and worsteds. The suds are passed through a screen box and patented flock catcher and then to a sump. The quantity of waste treated per day is 11,000 gal. The process used for grease recovery is the cracking method. Careful measurements, during which time 6,512 pieces, two-thirds woolen and one-third worsted, were scoured, showed 5 tons of flock recovered, 18 tons of oil used, 39 tons of soap used in scouring, of which half may be reckoned as oil, or 37.5 tons of oil were used; 46 tons of shoddy, or waste flock from carding, was sold, containing 30 per cent oil, or 13.75 tons; 17.5 tons of oil was recovered, or altogether 31.25 tons, or 83 per cent of that originally present in the waste. Following is the cost of recovery:

Interest, depreciation and operating expenses—	
7½ per cent on buildings.....	\$ 32.36
10 per cent on plant.....	129.21
Labor	167.89
Acid, sacking, etc.....	228.72
Steam	39.18
Total	\$597.36
17½ tons of oil.....	\$681.31
Returns—	
10 tons of pressed cake.....	11.60
Total	\$695.91
Profit for period during which 6,512 pieces were scoured	98.55

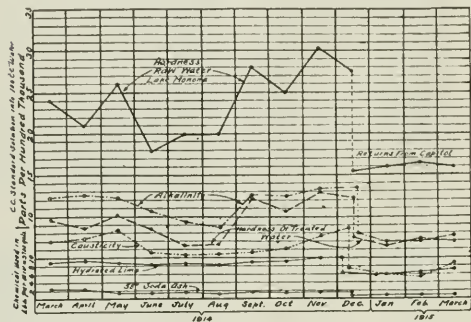
Under conditions in this country these profits from the grease recovery would not be anywhere as great and would probably not pay operation expenses. In the case of the Pittsfield and Barre plant in this country operating on heavy wool scouring waste there is very little profit above operating expenses, and as the grease to be recovered from the washing of cloth would be considerably less, the return would also be proportionately smaller.

Summary.—To sum up: The final disposal of the wastes from wool finishing processes necessitates the separation of those containing grease and oil and the recovery of this material by acid treatment, and the sedimentation and filtration through sand or cinders of this waste combined with the other wash waters. The acid waters from the grease recovery should be neutralized and then mixed with the other wash waters, treated by chemical precipitation and sedimentation, after which in some cases they may be diluted with clear water and used again in the mill or the effluent from sedimentation can be filtered through sand or cinders.

The Geological Survey now has available for distribution its annual statement on talc and soapstone in 1915. During the year 186,891 short tons of talc and soapstone, valued at \$1,891,582, were sold in the United States, an increase of 8 per cent in quantity and 1 per cent in value over the amount sold in 1914.

DATA ON THE USE OF THE WATER SOFTENER FOR BOILER FEED WATER.

In a paper presented before the Wisconsin Society of Engineers, Mr. H. R. Dorman gives some data on the results obtained from the use of a water softener system for treating feed water at the power and heat-

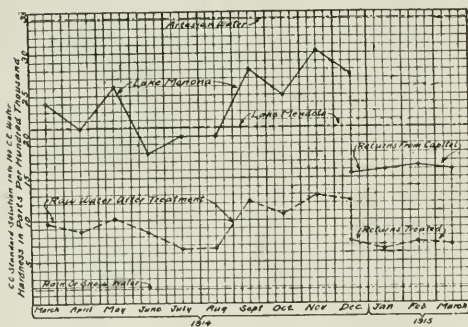


Relation Between Raw and Treated Water and Chemicals Used.

ing plant of the State Capitol at Madison, Wis. The following matter is taken from Mr. Dorman's paper:

The softener in use at the Capitol Power Plant is a top operated Northern Water Softener, of the cold process, continuous type, with a capacity of 96,000 gals. per 24 hours.

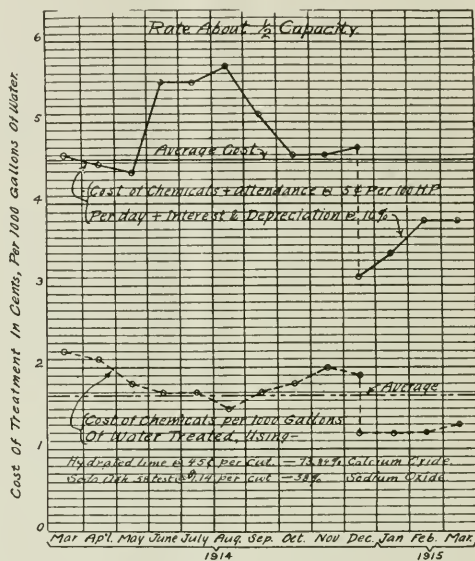
All water for station use is taken from Lake Monona through a 24-in. line about 1,800 ft. long,



Relative Hardness of Madison Water and Effect of Treatment on Monona Water.

extending about 500 ft. into the lake, and the normal submergence of the intake opening is 8 ft., to avoid drawing surface water or silt from the lake bed into the line. The water flows by gravity through this line into an intake well 20 ft. in diameter by 24 ft. deep, just outside the boiler house. From this well it is pumped by two 12x8x12 in. duplex steam pumps through a reducing valve (which maintains a pressure of 7 or 7.5 lbs.) directly into the operating mechanism, which is a small water wheel for stirring and feeding

the chemicals from the chemical tank, and also mixing the water and the chemicals in the downtake of the softener, thence into the tank. The chemical tank is above the main tank and has a capacity of 390 gals. For convenience in measurement and computation the tank is divided into 13 divisions of equal volume. The ratio of the mixture fed from the chemical tank to the total water passing over the wheel is approximately one ounce to the gallon. This is fed to the raw water by means of an endless bucket elevator discharging into a cup, thence through an orifice of known area



Operating Cost of Water Softener Per 1,000 Gals. of Water Treated.

to the downtake. A constant head is maintained above the orifice in the cup so that the discharge will be uniform at all times. After mixing, the water settles to the bottom of the downtake and rises on the outside to the discharge opening near the top of the softener. Precipitation occurs during this period, but any foreign matter that has not settled out is caught by an excelsior filter just below the water line. After treatment in the softener, the water passes to make up or storage tank, then to the open heater, then by the boiler feed pumps to the boilers.

During the heating season the return water from the heating system at the Capitol building supplies the boilers. This return is a mixture of condensed steam and cooling water and shows about one-half the hardness of the lake water. Hence there is a considerable saving on the chemicals used, and likewise in fuel, due to the higher temperature of the returns over that of the lake water.

The chemical tanks is charged once or twice in 24 hours, depending upon the quantity used. The quan-

ties of lime and soda ash necessary to recharge are determined by measuring the chemical mixture remaining in the tank. Tests of both the treated and the raw water are made every morning, and oftener if conditions seem to demand it. These are simple and quickly performed with the aid of a small testing cabinet furnished with the softener.

Portland Cement Industry in 1915.

Final figures on the Portland cement industry in 1915, gathered by the United States Geological Survey, confirm the estimate made on January 1, that there was a slight increase in shipments and a slight decrease in production. The shipments of Portland cement in 1915 were 86,891,681 barrels, valued at \$74,756,674 in bulk at the mills; the shipments in 1914 were 86,437,956 barrels, valued at \$80,118,475. The finished cement made in 1915 amounted to 85,914,907 barrels, which, compared with the 88,230,170 barrels made in 1914, shows a decrease of more than 2½ per cent.

The average factory price per barrel was 86 cents in 1915, compared with 92.7 cents in 1914, a decrease of 6.7 cents, or 7.2 per cent, in average price. According to the Survey's statement, prepared by E. F. Burchard, some of the commercial districts made a larger and some a smaller output than in 1914. Slight increases (less than 10 per cent) in output were reported from the Lehigh district and from most of the central districts; decreases were the rule in New York, Indiana, Illinois, and in the Rocky Mountain and Pacific Coast States. Increases of more than 10 per cent were made in the southeastern States, the largest increase, 20.3 per cent, having been made in the Tennessee-Alabama-Georgia district.

The shipments of natural cement in 1915 were 750,863 barrels, valued at \$358,627, a decrease in quantity of 422 barrels and an increase in value of \$7,257 compared with 1914. The average factory price per barrel reported for 1915 was 47.8 cents; the average in 1914 was 46.8 cents. The output in 1915 came from 12 plants, 4 in New York, 2 each in Ohio and Minnesota, and 1 each in Pennsylvania, Illinois, Indiana, and Kansas.

The shipments of puzzolan cement in 1915 were 42,678 barrels, valued at \$39,801, a decrease in quantity of 25,633 barrels and in value of \$23,557 compared with the shipments of 1914, both decreases being proportionately rather large. The average factory price per barrel reported for 1915 was 93.3 cents, compared with 92.6 cents in 1914. The output in 1915 came from 3 plants, 1 each in Alabama, Ohio, and Pennsylvania.

The annual statement of the Geological Survey on feldspar in 1915 is now available for distribution. During the year 113,769 short tons of feldspar, having a market value of \$629,356, was sold.

SOME CHEMICAL ASPECTS OF THE PEAT PROBLEM.*

By GILBERT T. MORGAN.†

Among the important matters overshadowed by the war is the perennial problem of the economical utilization of peat. Yet the question is one in which the belligerent countries are directly interested inasmuch as peat is found principally in high latitudes. Extensive deposits exist in Great Britain, France, Russia, Italy, Scandinavia, Germany and Austria. One-seventh of the total area of Ireland is covered by peat and enormous tracts of this deposit are found in Canada. For more than a century the problem has received the attention of numerous scientific investigators and has been attacked from many different points of view.

A SUGGESTED SOLUTION.

Only two years before the outbreak of war a practical solution of the problem was claimed for Germany by Dr. Carl Duisberg, a director of the color factory of F. Bayer & Co., Elberfeld, who at the Congress of Applied Chemistry held in 1912, at New York, stated his case in the following words:

The latest and most rational method of utilizing the peat or turf beds which are so plentiful in Germany and many other countries is practiced in Schweger Moor near Osna-bruck, according to a process discovered by Frank and Caro. There peat gas is produced and utilized and ammonia obtained as a by-product, the required power being generated in a 3,000-horsepower central electric power station. The moorland, after removal of the peat, is rendered serviceable for agricultural purposes.

At that place nearly 2,500 to 2,600 cubic meters of gas with 1,000 to 1,300 calories were obtained from 1,000 kilograms of absolutely water-free peat in the form of air-dried peat with 45 to 60 or 70 per cent of moisture. This gas represents energy equal to 1,000 horsepower hours, equal to 700 kilowatt hours, after deducting the heat and power used for the operation of the gas works. In addition 35 kilograms of ammonium sulphate was produced from the above quantity of peat, which contains 1 per cent of nitrogen.

The foregoing development appears to be a practical realization of the view held by many workers on peat in this country that the most economical use to make of this combustible is to convert it into gaseous fuel in suitable gas producers. Some of the earlier attempts at this solution of the peat problem are summarized in Professor Ryan's comprehensive reports on the Irish peat industries. (Economic Proc. Royal Dublin Soc., 1908, vol. 1, pp. 522-529.)

Other methods of disposing of peat must, however, be taken into account, such as the production of peat litter and peat molassine. Moreover, the recent epoch-making discoveries of Professor W. B. Bottomley (Ann. Botany, 1914, vol. 28, p. 531) on the application in agriculture and horticulture of bacterized peat or "humogen" will, when put into practice on an extended scale, lead to the utilization of large quan-

*From the Journal of the American Peat Society.

†Professor of Chemistry in the Faculty of Applied Chemistry, Royal College of Science for Ireland.

tities of turf. But nevertheless these outlets for peat will still leave available for fuel enormous quantities of turf, which should preferably be converted into gaseous fuel because by this process it becomes possible to recover certain valuable by-products.

GASEOUS FUEL FROM PEAT.

When peat is treated in a gas producer the products are combustible gas, ammonia, ash, tar and an aqueous distillate containing certain technically important organic compounds. The combustible gas, which is comparable in calorific power with that obtained from lignite, consists of carbon monoxide and hydrogen mixed with the non-combustible gases, nitrogen and carbon dioxide. The peat producer gas is generally free from sulphur, the absence of this element being of great advantage in a gaseous fuel used in iron and steel industries and in the manufacture of glass and ceramic wares.

At present the only plant of this description in Ireland is the gas producer furnishing the gaseous fuel for the gas engines of the factory of Messrs. Hamilton Robb, Ltd., of Portadown. It is of interest to note that although on account of the comparatively small capacity of the plant no attempt is made to recover and utilize any by-products, yet, nevertheless, this installation has proved to be a financial success. There can be little doubt that in a scientifically controlled plant, large enough to render practicable the recovery of ammonia and other by-products, the economy effected would be considerably greater.

BY-PRODUCTS FROM THE PEAT GAS PRODUCER.

Ammonia.—Peat may contain 0.5 to 2.5 per cent of nitrogen, and in recent years considerable improvements have been made in the way of increasing the yield of ammonium sulphate recoverable from this combined nitrogen.

By passing steam over peat heated to 350° to 550° almost the whole of the nitrogen is obtained as ammonia (Caro, Chem. Zeit, 1911, vol. 35, p. 505). With a peat containing 50 to 70 per cent of water and 1.05 per cent nitrogen, Frank, by operating on 50 to 60 tons of wet peat at a time, obtained 90 pounds of ammonium sulphate per ton of peat. This yield corresponds with 77 to 80 per cent of the total nitrogen.

Caro has raised the yield to 85 per cent of the total nitrogen working on peat containing 60 per cent of water.

Similar improvements have been embodied in the modern types of Mond plant so that now it is possible to recover the greater part of the nitrogen of peat in the form of the valuable fertilizer, ammonium sulphate. The other commercial nitrogenous fertilizer is sodium nitrate, a substance also required in the manufacture of nitric acid as a starting point in the production of explosives and synthetic dyes. The importance of increasing the output of ammonium sulphate from peat lies in the circumstance that this salt can displace sodium nitrate as a nitrogenous manure,

thus rendering the nitrate available for the manufacture of explosives and other chemical products.

For the four illustrations of producer plant specially designed for the gasification of peat with ammonia recovery The Power-Gas Corporation, Limited, of Stockton-on-Tees, in 1905, first turned its attention to the gasification of peat with ammonia recovery and has obtained the extremely favorable results tabulated below:

Fuel used.	German Peat per cent.	Italian Peat per cent.	English Peat per cent.
Moisture content of fuel.....	49 to 69	15	57.5
Nitrogen content of fuel.....	1.0	1.58	2.3
Quantity of gas produced per ton of theoretically dry peat, cu. ft.	85,000	60,000	90,000
	B.t.u. per c.f.	B.t.u. per c.f.	B.t.u. per c.f.
Heat value of gas produced.....	150	166	134
Sulphate of ammonia produced per ton of theoretically dry peat	70 lbs.	115 lbs.	215 lbs.

The Simon-Carves By-Product Coke-Oven Construction and Working Company, Limited, have made large-scale experiments on the gasification of peat in Moore gas producers. Very favorable results were obtained, and for the data of a seven days' test on Norfolk peat I am grateful to Mr. J. H. Brown of this company. Peat, containing 63 per cent of moisture and with a nitrogen content of 2.235 per cent, yielded per ton 94,850 cubic feet of gas (100 B. t. u. per cubic foot) and 168 pounds of ammonium sulphate. A longer run would certainly have given even more of this salt.

These experiments confirm the claims made by Dr. Duisberg, and demonstrate conclusively that peat containing a high proportion of moisture can be gasified so as to yield a gas fuel of high caloric value with a good recovery of nitrogen in the form of ammonium sulphate.

Peat Ash.—Peat differs from wood in yielding on combustion a comparatively large and variable proportion of mineral ash, the amount varying from 5 to 15 per cent.

There are very few published analyses of the ash of peat. A determination of the constituents of the ash of a moss peat from a high moor in the Canton of Zurich, Switzerland, made in 1850 by H. Bohl (Dinglers Journal, vol. 153, p. 223), showed that the ash contained the oxides of aluminum, iron, and calcium, existing to a considerable extent in the form of carbonate, sulphate, silicate, and phosphate. The ash also contained a very appreciable amount of alkalies, with a preponderance of potash.

As the peat ash must consist in part of those mineral constituents of the soil originally assimilated during the growth of the peat vegetation it may fairly be assumed that the ash constituents would act beneficially when restored to the land rendered available for cultivation by the removal of the peat. This applies especially to the potash and phosphate present in the peat ash. By using the peat ash as a dressing for the recovered land the potash locked up in peat would

be rendered available for agriculture at a time when the shortage of this alkali is felt very acutely.

Peat-Producer Tar.—The incomplete combustion of peat in the producer leads to the formation of a certain proportion of tar which is collected in the hydraulic scrubbers of the plant. As the result of many trials made at the fuel-testing station at Ottawa it was concluded that the tarry components of the gas evolved in the upper zones of suitable producers could not be entirely burnt or split up into permanent combustible gases. The condensation of a certain amount of tar is unavoidable, and special means of removing this by-product must be adopted.

The amount of tar produced yearly in the Portadown plant is about 100 tons. Samples of this waste product were examined in the chemical laboratories of the Royal College of Science for Ireland, when the results showed that a fractional distillation of the tar resulted in the isolation of substances of industrial importance.

A greatly increased output of the peat tar is, however, the first essential step towards commercial success in this direction. This increase would result naturally from the installation of large plants for the gasification of peat or from an increase in the number of factories using gas derived from peat. Ten installations comparable in size with that of Messrs. Hamilton Robb, Ltd., would yield approximately an annual output of 1,000 tons of peat producer tar, a quantity which would furnish a practical basis for the industrial exploitation of the derivatives of this tar.

Many experiments have been made in the distillation of peat and on the fractionation of the resulting peat tars, but the results, which are summarized in Professor Ryan's instructive report, indicate that our knowledge of the chemical nature of the products is far from complete (loc. cit. p. 516, compare Dvorkovitz, Jour. Soc. Chem. Ind., 1894, vol. 17, p. 596). The older distillations were not made under conditions comparable with those obtaining in gas producers, but in spite of this difference the products of the fractional distillation of the respective tars appear to be somewhat similar.

In the experiments carried out by myself and Mr. G. E. Scharff (Economic Proc. Royal Dublin Soc., 1915, vol. 2, pp. 161-167) distillation of the moist crude producer tar effected a separation of certain volatile oils from a non-volatile bituminous material (crude pitch) amounting to about 17 per cent of the total tar. By heating the crude pitch to 122° C. and pouring off the liquid portion about 6 per cent of a refined soft pitch could be separated from a solid friable carbonaceous residue.

This pitch, either alone or mixed with the carbonaceous matter, could be used as asphalt, as a caulking material or as an insulator in electrical work. The carbonaceous matter could be utilized separately as a self-briquetting combustible of high calorific value.

VOLATILE OILS FROM PEAT TAR.

The moist peat producer tar contained about 29 per cent of water and yielded on distillation 50 per cent of volatile oils. The latter by further treatment were separated into neutral oils, waxes, and acidic oils.

Acidic Oils.—The last of these fractions was obtained by extracting the crude distillable oils with dilute caustic soda and reprecipitating the acid oils from the alkaline extract by means of a mineral acid. Fractional distillation of the acidic oils showed that these substances consisted principally of complex phenolic compounds. Attention was specially directed to these substances as they seemed likely to afford material for the manufacture of useful disinfectants comparable in efficiency with lysol, creolin, cyllin, and other coal tar disinfectants.

PEAT DISINFECTANTS.

It was formerly known that peat tar contained substances having antiseptic properties, but these compounds had hitherto neither been isolated nor standardized (compare Ryan loc. cit. p. 514; Szek, Eng. Pat. 15606, 1902).

The well known Rideal-Walker test for disinfectants and the modified procedure devised by Martin and Chick afford methods for controlling quantitatively the separation of the germicidally active acidic oils from peat tar, and for ascertaining the bactericidal value of these acidic oils. Phenol and the cresols are segregated in the fraction boiling below 200° C., which is about seven times as toxic as phenol itself towards *Bacillus typhosus*. The fraction of acidic peat boiling at 200° to 250° is 17 times as active as phenol (carbolic acid) on the same pathogenic organism.

The most intense germicidal activity is possessed by the fraction of acidic peat boiling at 253° to 360°, for this product has a phenol (carbolic acid) coefficient of 31. (Morgan and Scharff, Eng. Pat. 19,253, 1914.)

These results show that by distillation and simple chemical treatment of the oils obtainable from peat producer tar one can, under appropriate bacteriological control, isolate oils of intense bactericidal activity suitable for the manufacture of antiseptics, disinfectants and germicides. When it is remembered that phenol (carbolic acid), the standard disinfectant of this type, is greatly required in the manufacture of explosives (lyddite), drugs (salicylic acid, aspirin, etc.), as well as for many other synthetic products, it will be readily realized that these peat disinfectants would be welcomed as efficacious substitutes for carbolic acid, if they were forthcoming in sufficient amount, especially at the present time when antiseptics are so urgently needed.

These fractionated germicidal oils can be employed either severally or in varying combinations in the manufacture of antiseptics, disinfectants, and germicides. For this purpose they may be used either in a concentrated form or diluted with organic solvents. These oils are sparingly soluble in water and can be used in

suspension in this medium. They can also be employed in emulsified condition, the emulsification being produced by their intimate mixture with gum acacia mucilage, castor oil soap, or other well known emulsificants.

These germicidal oils can also be made up into solid disinfectants by mixing with hard soap, cane sugar, milk sugar, dextrine, starch, gums, resins, or with porous materials such as fuller's earth, infusorial earth, gypsum, powdered chalk, or whiting, slaked lime, animal charcoal, wood charcoal, or other absorbents.

NEUTRAL OILS FROM PEAT TAR.

The neutral oils left after extracting the germicidal acidic oils with alkali were purified by fractionation when the lower fractions were obtained as clear pale yellow liquids darkening rapidly on exposure to the atmosphere until they become dark brown and almost opaque. During this process the oils absorb a considerable proportion of atmospheric oxygen.

The foregoing neutral oils could be used as lubricants, as liquid fuel, for example, in Diesel engines, and when mixed with the pitch from peat tar would furnish a refined tar.

The chemical reactivity of these neutral (nonacidic) oils shows that they do not consist wholly of members of the paraffin series. Their exact relationship to other hydrocarbon series is not known with certainty and they would certainly repay further investigation.

WAX FROM PEAT TAR.

The higher fractions of the neutral oils boiling above 250° C. deposit on cooling considerable quantities of crystalline solid. This material, when drained and dried, is an almost colorless wax melting at 35° to 40° C., and would serve as a promising starting point for the manufacture of candles.

AQUEOUS DISTILLATE FROM PEAT TAR.

The aqueous distillate from the producer contains in addition to ammonia certain organic substances soluble in water, among which have been recognized methyl alcohol, acetone, acetic acid and its immediate homologues, and pyridine bases. All these compounds are of industrial importance. Methyl alcohol is an important solvent and the starting point for formaldehyde. Acetic acid and its homologues are required for the manufacture of acetone and other ketones. Acetone is an important solvent used in considerable quantities in the manufacture of the explosive, cordite. The pyridine bases are pungent liquids useful both as solvents and as disinfectants. The recovery of these compounds could be rendered practicable by suitably modifying the condensers and scrubbers of the peat producing plant.

SUMMARY.

1. Peat has long been employed as a domestic fuel. Its industrialization could be most efficiently brought about by gasifying it in gas producers, as this procedure would render feasible the recovery of several valuable by-products.

2. The combined nitrogen of the peat can be eco-

nomically recovered in the form of ammonium sulphate. This valuable fertilizer, together with the peat ash containing potash and phosphoric acid, could be restored to the land from which the peat has been taken.

3. Peat tar, another by-product, can be fractionated into the following useful materials: refined pitch and tar, candle wax, lubricating and burning oils, and very powerful disinfectants, greatly exceeding carbolic acid in germicidal strength.

4. The aqueous distillate from the producer contains methyl alcohol, acetone, pyridine bases and crude acetic acid, all of which are capable of recovery and utilization.

The economical utilization of peat in the generation of gaseous fuel, even without recovery of by-products, is today an accomplished fact. It can scarcely be doubted that, with efficient chemical control, a larger plant of sufficient capacity to deal rationally with the ammonia, tar, and other products of the destructive distillation of peat would lead to still greater economies in the employment of this important combustible.

Asphalt Industry in 1915.

The asphalt industry as a whole was prosperous in the year 1915, according to a statement just issued by the United States Geological Survey. The natural asphalt, including grahamite, gilsonite, elaterite, and bituminous rock, produced and sold at mines and quarries in the United States in 1915 amounted to 75,751 short tons, valued at \$526,490. Though this quantity was 5 per cent less than the output in 1914, the reports of the sales of manufactured asphalt derived from petroleum of domestic origin disclose a gain of 84 per cent over the quantity sold in 1914. The total sales of manufactured asphalt amounted to 664,503 short tons, valued at \$4,715,583. In addition to this output, refineries in the United States made and sold 388,318 short tone of asphalt, valued at \$3,730,436, that was derived from petroleum imported from Mexico.

The decrease in the output of natural asphalt is confined to bituminous rock and is due largely to the keen competition that this type of asphalt is forced to meet in its chief market—the paving industry—with manufactured substitutes.

Statistics just completed under the supervision of J. D. Northrop, of the Geological Survey, show that of the quantity of manufactured asphalt derived from domestic petroleum in 1915 a total of 417,859 short tons, valued at \$2,392,576, was marketed as road asphalt and flux, and 246,644 short tons, valued at \$2,323,007, as residual pitch, used chiefly for paving.

The output of the Mexican product in 1915 may therefore be subdivided into road asphalt and flux—174,854 short tons, valued at \$1,325,201—and residual pitch—213,464 short tons, valued at \$2,405,235.

APPRAISALS AND DEPRECIATION OF FERTILIZER PLANTS.*

By W. S. RANKIN.†

Some of you are no doubt familiar with the subject of appraisals, but there are others of you to whom this subject is a more or less unfamiliar one. I believe that if you have in the past dismissed the subject with only a passing thought, that it was because it has not been brought to your attention in the light of its very real interest to you. And I trust as we make a brief survey of this very interesting subject today, that you will find something which will not only interest you, but something which will either now or at some future time prove of real value to you.

Every one within the sound of my voice will agree that a knowledge of the actual physical value of any property is a very desirable thing to have, and it is not only desirable, but it is also very valuable information.

There are some of you who have in the past, no doubt, wished for actual information concerning physical values. Maybe it was because such information would have been of value to you in establishing a fair buying or selling price for a piece of property, perhaps it could have been valuable in negotiating a loan or as a basis of a statement to your banker or to your stockholders, or valuable as the basis for a stock or bond issue. Also the knowledge of physical values is very useful information in establishing a basis for forming or dissolving partnerships, for settling estates and establishing financial connections of all kinds. It is necessary information if you desire to intelligently place and distribute your fire insurance, and in case of fire, you must know and be able to prove these physical values if you desire to collect full insurance on all items destroyed.

A clear knowledge of physical values and depreciation is necessary if you desire to correctly figure your manufacturing costs. In fact, it has to do with nearly everything relating to the safe conduct of your business.

As stated a few moments ago, you will no doubt readily grant the many uses for a knowledge of physical values, but some of you will immediately assert that you are already thoroughly familiar with such values, and others of you will imply the same thing by making the question "What reason is there for my having lost sight of the physical values of my plant?" and so first of all let us study briefly the subject of physical values, and we will then have a clearer understanding of appraisals.

Let us first ask the question "What are some of the ways in which we lose sight of physical values?" and then after considering this question we can better answer the question, "What is an appraisal?"

Now to commence at the very beginning of this matter, let us first ask if all of you are sure that the values as originally set up on your books, the values on which all subsequent statements must be based, are in all respects the correct values? Then after you have satisfied yourselves regarding the correctness of original values, turn with us for a few moments and let us study briefly the changes in physical values, for physical values are changing. There are reasons for these changes, which changes either separately or combined, are apt to soon make your book account of values misleading. Therefore let us look at this subject of values from four standpoints:

- 1st. Influences bearing on original cost of plant.
- 2nd. Mechanical changes in the plant.
- 3rd. Changes in the value of materials, labor and equipment entering into the plant.
- 4th. Depreciation.

INFLUENCE BEARING ON ORIGINAL COST OF PLANT.

Granting that your plant, to start with, was a new one. Was the first cost as set up on your books a fair one? That is, was the cost a value that would hold under normal conditions?

To correctly distribute all expenditures incurred by a company just commencing business is not always an easy task, and besides for business reasons of their own, a concern may handle the distribution of such costs in a manner to best suit their convenience. So it is even with a new plant the question can arise, whether there are no items charged against the plant account which did not rightly belong there, and on the other hand, were there no charges overlooked or omitted which were legitimate charges against the plant account?

Maybe instead of building a new plant the property we are considering was secured by purchase or there was a consolidation of interests. In such cases the price paid for the property, or the value placed on it in the consolidation did not necessarily represent the actual physical worth of the property. The property may have been secured at a very cheap price, or due to the business controlled, or possibly for other business reasons, the price paid was far greater than the physical values involved. So in either case there was at the beginning no accurate knowledge of physical values.

MECHANICAL CHANGES IN THE PLANT.

In every operating plant changes are constantly being made. Changes even though small in themselves, when they are made year after year, will finally make a serious physical change in any property.

With respect to building changes, there may be some buildings torn down, some entirely remodeled, some added to and some new ones constructed. With respect to changes in machinery and equipment, there are alterations, additions, removals, changes in types and sizes of machines, changes in system and processes of manufacture, changes in methods of handling

*Paper presented at the annual convention of the National Fertilizer Association, July 12-14, 1916.

†General Manager Appraisal Company of the South, Savannah, Ga.

goods, possibly a change from steam to electricity for motive power.

For a while a careful accounting may show a fairly accurate record of these changes, but as they go on year after year, errors will most certainly creep in. For example: A change is made in the plant; you are called upon to decide how much of the cost of the change is chargeable to permanent improvements and how much to the repair account. A difference of opinion often prevails as to the correct division of this cost, or it is left to some bookkeeper to make an arbitrary division, or maybe some mechanic who has no real knowledge of the difference between the two accounts, "Permanent Improvements" and "Current Repairs" will be called upon for the division of costs, which he is apt to make in the least troublesome way.

Possibly some of you have seen new machinery and equipment bought during a year of good business, and its cost charged to operating expense, not to plant account.

Have you ever seen a piece of work done and either because no appropriation could be secured, or because the appropriation was too small, a large part of what was really an improvement, went into the books under some other head? The cost unloaded on some other job, hidden by being charged to "Repairs" or to "Operating" or to some account other than to "Improvements," where it really belongs.

Another great source of inaccuracy in keeping track of physical values is in the cost of installation, and in the labor cost of work done by the regular mechanical force employed at the plant. Machinery is bought and installed, millwright work done, expensive repairs and alterations made, and this work is often handled by the regular force of mechanics and the labor cost of same entirely overlooked, or often when the work is handled by the regular men, the job is not charged with the labor cost at all, or maybe because the work was very necessary work, the job was loaded down with costs other than what belonged to it.

When any building or any installation is remodeled or rearranged, the cost is nearly always greater than if the work had been done in that way to start with; and there is then an uncertainty whether the permanent investment has been increased or diminished by the change, and if either by how much has it been changed. Recently I had a manager tell me that a certain piece of work had cost him \$14,000, but I soon found that they did not want to shut the plant down while making certain changes, and so the installation made while the plant was operating had cost an additional \$6,000, or about 75 per cent more, than it would ordinarily cost.

And so it is, that due to those and many other reasons, mistakes creep into my set of books, and no system of accounting can for any length of time, keep a true record of the changing value of a plant.

Then we have another change of values to consider,

and this change brings us to the third of the reasons we have for changing physical values, that is,

THE CHANGES IN THE VALUE OF MATERIALS, LABOR AND EQUIPMENT.

In the past ten or fifteen years there have in many cases, I think I am safe to say in most cases, been very material changes in the cost of machinery and equipment and of lumber and building materials; also in many cases there have been changes in the wages paid both skilled and common labor. These different changes mean of course, that a plant built a number of years ago, could not in most cases, be duplicated today for what it originally cost. On the other hand it is possible that the property may have originally cost more than it would cost to reproduce it today.

Sometimes it is the case that due to some person's ability as a trader, or their foresight in taking advantage of certain local and special conditions existing at the time, that the original cost of a property was far below its reproductive value under normal conditions. On the other hand local and special conditions may have operated to increase the cost of a plant over that of normal times, and there are often cases where for business reasons large sums are paid in the form of overtime wages or as a bonus, these extra sums being paid in an effort to have the work completed by a certain time.

I have in mind one installation in a manufacturing plant that cost 60 per cent more than its contract price, due solely to the payment of bonuses to manufacturing companies for the prompt delivery of equipment and also to the payment of overtime wages for installation, all of which were paid in an effort to complete the work by a certain date.

In speaking of this subject of increased cost of materials, I do not refer to exceptionally high prices due to abnormal conditions, an illustration of which even now exists, but I desire to call your attention to the increase in cost of almost all machinery and equipment during the past few years. There has not only been abnormal increases in some cases, but also an increase in nearly every class of machinery and equipment. Some abnormal prices will go down again when certain unfortunate world events are adjusted, but it can hardly be assumed that all prices are going back to the level of several years ago.

The managers of two large machinery manufacturing plants have recently told me that they could not see where it was possible for the prices of machinery to go down at all within the next two years, and two years is as far ahead as anyone could dare hazard an opinion.

Just here let me call your attention to one abnormal increase and its affect on your values, and that is the advance in the price of lead. It is very probable that some of your acid plants were built when lead was five or five and a fraction cents per pound. Today lead is around nine and one-quarter cents per pound. It may be your judgment that the price will fall again,

but will you attempt to say how long before it will go back and how far. And in the meantime if you should have a fire will your present insurance cover your loss. Possibly some of you have already taken out additional insurance to cover this increased value, and maybe some of you will not care to do so, that is a matter for you to decide. I have only mentioned this for your consideration and in this connection will also remind you of the increases in wages paid to lead burners, an increase from \$7.00 and \$7.50 to \$14.00 and \$15.00 per day at the present time.

Now let us turn to the fourth cause for changes in physical values, which bears not only a very close relation to all physical values, but it must be taken into consideration if you desire to correctly figure your costs of production.

DEPRECIATION.

The loss in value, whether tangible or intangible, whether resulting from physical decay or obsolescence, is what constitutes depreciation.

Let us be frank in recognizing that the amount of depreciation cannot in every case be definitely determined, but this does not for one moment conflict with the fact that there is depreciation.

A great many people make no distinction between efficiency and depreciation. Because a plant or a machine is efficient they claim it has not depreciated. True, an old machine may run more smoothly than a new one, but this is only another reason why we must distinguish between efficiency and depreciation. Somewhere I have read the following distinction between these two—"Efficiency is the test of present day effectiveness. Depreciation is the slow process by which an industrial plant, what its present effectiveness may be, gradually approaches the time of discard and replacement.

Depreciation is ever present; if you eliminate depreciation in any building or machine you at once give that thing a life for all time. If a building or machine did not depreciate there would be no necessity for repairs and upkeep. Some of you may state, and I have seen some manufacturers so figure, that repairs and upkeep eliminate depreciation. But if that manufacturer was offered the choice of two plants of the same size and type, one of them ten years old and the other brand new, have you much doubt as to which plant he would select.

Even with current repairs and renewals met, there is a certain amount of depreciation which cannot be eliminated except by the replacement of the entire plant, because replacements and repairs do not restore the whole plant to its original value, they only keep it from becoming less valuable.

Appreciation due to the increased costs of material and labor may in certain cases counterbalance for a time the loss suffered by depreciation. But that is a matter belonging to the change in value of materials, of which we have just spoken, and it does not alter the fact of depreciation.

The first question often asked by some manufacturers is: "How much should I charge off for depreciation." Now depreciation does not result from one cause, but many causes, it is a hard thing to arbitrarily gauge, and an arbitrary charging off of some sum on your books will not settle the question of depreciation and present value.

In accounting, the sum charged off for depreciation is most often an arbitrary one, with some manufacturers it is largely controlled by the profits of the year in which the charge is made. Others, for business and private reasons, desire to either keep their plant values up or to keep them down, and as a result they soon lose sight of what their physical values really are. The same reasons which often effect the amount of depreciation allowed will sometimes have an influence on whether certain expenditures are charged to permanent improvements or to the repair account.

When a machine, which has been transferring its value into goods for ten or twenty years finally gives out, the cost of its replacement does not belong to current repairs, and if it is an expensive machine and no reserve has been set aside to take care of such replacements, the cost of its replacement may unduly burden the year's business in which its replacement has to be met.

You have an illustration of the point I am trying to bring out, in the operation of your sulphuric acid plants. In them you keep up the repairs each year, but eventually you have got to shut the plant down and rebuild it. That cost or rebuilding is not a charge solely against the year in which it occurs. The depreciation which finally makes this rebuilding expense necessary, has not occurred all in one year; it has been going on year after year, and repairs and upkeep could not eliminate it, and if you have distributed all of your profits each year without setting aside something beyond the amount of current repairs, that is if you have not built up some reserve to take care of this extraordinary expense, you are going to load one year's business down with a very heavy charge which does not belong to it.

In this example of sulphuric acid plants you can see where depreciation effects manufacturing costs. It may be that twenty-five cents per ton of acid produced will cover the current repairs necessary in the acid plant, but if you were to figure your selling price to cover only actual cost of production with a small margin of profit, and in this cost of production you included the cost of current repairs as covering the total cost of depreciation of the acid plant, then you will at the end of ten or twelve years find yourself with a large expense for rebuilding the plant; burners, towers and acid chambers must be rebuilt either in whole or in part, and probably at a cost of twenty or thirty thousand dollars, which will mean an additional expense of about fifty cents per ton of acid produced through all the years of operation, and this expense coming all in one year could be a very serious embarrassment to

some dividend accounts, especially if the year had been a poor one in other ways.

The same depreciation which is going on in your acid plant is going on in every other department of your plant, and in every manufacturing plant, and if account is not taken of depreciation and a reserve is not built up sufficient to make the necessary replacements when desired, then you will find that some day this subject of depreciation is going to demand the notice that you will not now give to it.

There may be cases in very extensive plants, with a great many and varied styles of buildings and machines, where it is possible for the expenses of replacements due to physical decay, inadequacy and obsolescence, to be fairly well distributed from year to year, but in the average plant those items of so large an amount as to burden the year in which they are met, cannot be classified as "Current Repairs," but should be provided for under their proper head of depreciation.

Depreciation can be divided into "Unit" and "Composite" depreciation.

Unit depreciation or the decay of individual units, increases from zero to one hundred per cent. Composite depreciation which is the resultant upon the whole plant of all the unit depreciation, will not in an operating plant go beyond a certain percentage, for as an operating proposition you could not turn out either the quantity or quality of goods if composite depreciation went beyond a certain point. Of course in an idle plant composite depreciation can go on and on, the same as unit depreciation does.

Again depreciation viewed from the point of its cause may be the result of either or both physical and functional decay. You of course are familiar with physical decay, then again a machine may not have depreciated physically or mechanically, but some discovery or invention may have rendered it obsolete, or at least not so desirable a type of machine as it originally was. Whichever is the greatest, physical or functional depreciation, that one is effective in determining depreciation, but the two should not be added together.

There is a depreciation due to a machine no longer being fully capable of performing the work for which it was intended. It may not have depreciated from a mechanical standpoint, or from the point of obsolescence, but if the service can be bettered in the case of inadequacy, then there is a depreciation which should be taken into account.

Even in unit depreciation the question of salvage must be taken into consideration in estimating the total depreciation of any unit, for beyond the salvage value the depreciation will not pass. You have an example of salvage value in acid plants; there is always a salvage value in the old lead; so in a great many other cases the salvage value must be taken into consideration in estimating depreciation.

Every manufacturer should make reservations to

insure the preservation of capital, creating a fund for ultimate replacements, and the value of a plant at any particular time is theoretically the reproductive value less the replacement fund accumulated at that time, but seldom does present value plus the replacement fund even approximate the cost of reproduction, because as I have pointed out there are so many different ways for errors to creep in.

The present value of any plant can only be accurately determined by an appraisal. You keep an account showing all transactions in stock during the year, but nevertheless you do not trust your books as showing the stock on hand, but each year make an inventory of such stock, and is it wise in view of the reasons we have outlined, to trust your books year after year for physical values or would it be wise to occasionally make an inventory of your physical plant also. That is what an appraisal is—an actual inventory of the physical plant.

An appraisal, if it is to carry weight, to prove values, cannot be an estimate to values, it must be thorough. It must be built up item by item, showing all of these things which influence cost, everything listed and priced in detail, showing in every feature the fairness and accuracy of all claims which are based on the values which the appraisal establishes.

An appraisal must show every machine, the manufacturer's name, size, type and all attachments which influence its cost. The price of each machine must be shown, freight and installation costs figured for each machine, with a description of all millwright work and cost of same, and with allowance for all local and special conditions which will have any influence upon the cost of installation. In fact all items of building construction, machinery, equipment, etc., must be carefully inventoried and each item priced as outlined, if your appraisal is to carry weight and be of any real value.

All values should be figured first on a reproductive new basis. That is, you must first show what it would cost to reproduce your plant new. Then after determining reproductive new value, we must determine the depreciation of each unit.

Not an arbitrary depreciation made solely for the purpose of creating a fund for ultimate replacement, but we want to determine actual depreciation for the purpose of determining present sound value.

The way to determine actual depreciation is by inspection. Two plants of the same type and age may now show the same depreciation at the end of a given time. There are many reasons for this discrepancy. One manufacturer will make both prompt and thorough repairs, thus keeping his plant in good condition, while another manufacturer will spend just as little on repairs as is possible.

So the extent of repairs and the promptness with which they are made bears an important relation to depreciation.

Another very important factor in determining de-

preciation is the type and equality of construction. Some plants are of cheap construction, cheap materials, cheaply put up. Some of light construction, maybe too light for the class of occupancy, while other plants are built of the best materials, built substantially and built to last, therefore each building can only be intelligently depreciated after a personal inspection of its condition.

And what is true of buildings is also true of machinery and equipment. Machines of different types do not depreciate the same, and even machines of the same size and type will not show the same depreciation at the end of any given time. For example, in one plant there will be twenty-four burners on a Glover tower, while another plant will have thirty or thirty-six burners on the same size tower. You can readily see that the life of these two towers will not be the same. Again, one plant will make on an average of 300 mixings a week, while in another plant 800 mixings are made, which means a difference in the wear and tear on the mixer.

If a plant is shut down depreciation is an entirely different proposition from what it is in a plant which is in operation. This is readily seen in the case of lump burners, in which the depreciation when shut down, is greater than if the burners were in operation.

The worth of a building or a machine at some particular time in its life does not necessarily have much bearing on its ultimate cost of replacement, due to the many influences acting upon it, though for some individual units, such as an acid egg, we must, in figuring depreciation depend largely on the average life of that class of equipment.

And so we find that in almost every case, after the reproductive new value is determined, personal inspection is the only way to determine depreciation, and that means the present sound value of the property.

These different cases have been referred to for the purpose of illustrating to you a few of the things which must be taken into consideration in making an appraisal, and now just one thing more before closing. Every man, even though a good superintendent or a good engineer, is not therefore fitted to qualify as an appraiser. You do not study medicine to doctor yourself, and in the same sense when you undertake an appraisal, it must, to be of real value, be made by a man or men trained in appraisal work and also made by a disinterested party; one with no interest in the values of the property being appraised.

While an appraisal is often made with some particular purpose in view, it can at the same time be made so that it will answer all purposes. The appraisal may be wanted at the time for financial purposes, but at the same time all values should be separated, showing the values for each building or unit and the value of machinery and equipment in each building, also, uninsurable values should be separated from insurable values. Thus you are not only fur-

nished with an appraisal for financial purposes, but there is a division of values which will be of service in figuring manufacturing and overhead costs for each department. There is also a division showing the proper distribution of all insurable values, thereby enabling you to place a proper amount of insurance and to correctly distribute same, and in case of loss by fire you will not only have all values properly covered by insurance, but the appraisal will then furnish the details of the loss. It is your proof of loss, and it will assure you the collection of a just amount of insurance on every item destroyed. And besides saving you a possible financial loss, it will facilitate a prompt adjustment of the loss, which is often almost as important as the collection of the full insurance. An appraisal also inspires confidence in the man whose good judgment and sense of fairness has prompted him to provide an appraisal.

No company should allow its properties to waste without making adequate provision for replacement, and the integrity of all investments rests upon a clear distinction between capital and revenue, and with both of these matters, the subject of depreciation and physical values is closely interwoven.

I have tried to point out to you a few of the ways where a correct knowledge of physical values is necessary to the correct conduct of a business. I sincerely trust that I have brought to your attention some thought which may be of value to you either now or at some time in the future and if I have not made myself clear on any point, it will be a pleasure for me to give all further information and assistance which it is in my power to render.

Kelp Industry at Sydney, B. C.

A U. S. Consular Report states that the Canadian Potash & Algin Co. (Ltd.), organized in 1915 with a plant at Sydney, B. C., is now utilizing from 30 to 40 tons of raw kelp daily in the manufacture of fertilizer. The product is a fine, dry, but heavy powder. Plans are being made to enlarge the plant and install special machinery for the extraction of other materials from kelp. Algin, which will be made one of the specialties of the local plant, is said to possess a viscosity many times greater than that of starch or gum arabic. The chief use of algin is for the sizing of fabrics, the effect being to give the material treated the appearance of waterproof sheeting, but leaving it more elastic than when treated by other customary waterproofing materials. An act relating to the licensing of kelp-reduction works, designed especially to encourage the development of the industry and for the protection of persons or companies desiring to engage in the business, was passed by the 1915 session of the Provincial legislature. The industry is under the jurisdiction of the Minister of Fisheries. A license protects the operation of any reduction factory for an area extending 50 miles along the coast.

REVISED STANDARD TEST FOR PENETRATION OF BITUMINOUS MATERIAL.

A proposed revised standard test for the penetration of bituminous material was submitted at the recent annual meeting of the American Society for Testing Materials by the Committee on Road Materials, of which L. W. Page is chairman and Prevoost Hubbard, secretary. The test is designed to supersede the present standard test. The committee recommended that the standard be referred to letter ballot of the society for adoption. This proposed revised standard test was as follows:

Definition.—Penetration is defined as the consistency of a bituminous material, expressed as the distance that a standard needle vertically penetrates a sample of material under known conditions of loading, time and temperature. Where the conditions of test are not specifically mentioned, the load, time and temperature are understood to be 100 g., 5 seconds, 25° C. (77° F.), respectively, and the units of penetration to indicate hundredths of a centimeter.

Apparatus.—The container for holding the material to be tested shall be a flat-bottom, cylindrical dish, 55 mm. (2 3/16 in.) in diameter and 35 mm. (1 3/8 in.) deep.¹

The needle² for this test shall be of cylindrical steel rod 50.8 mm. (2 in.) long and having a diameter of 1.016 mm. (0.04 in.) and turned on one end to a sharp point having a taper of 6.35 mm. (1/4 in.).

The water bath shall be maintained at a temperature not varying more than 0.1° C. from 25° C. (77° F.). The volume of water shall be not less than 10 liters and the sample shall be immersed to a depth of not less than 10 cm. (4 in.) and shall be supported on a perforated shelf not less than 5 cm. (2 in.) from the bottom of the bath.

Any apparatus which will allow the needle to penetrate without appreciable friction, and which is accurately calibrated to yield results in accordance with the definition of penetration, will be acceptable.

The transfer dish for container shall be a small dish or tray of such capacity as will insure complete immersion of the container during the test. It shall be provided with some means which will insure a firm bearing and prevent rocking of the container.

Preparation of Sample.—The sample shall be completely melted at the lowest possible temperature and stirred thoroughly until it is homogeneous and free from air bubbles. It shall then be poured into the sample container to a depth of not less than 15 mm. (5/8 in.). The sample shall be protected from dust and allowed to cool in an atmosphere not lower than 18° C. (65° F.) for one hour. It shall then be placed in the water bath along with the transfer dish and allowed to remain one hour.

Testing.—In making the test the sample shall be

placed in the transfer dish filled with water from the water bath of sufficient depth to completely cover the container. The transfer dish containing the sample shall then be placed upon the stand of the penetration machine. The needle, loaded with specified weight shall be adjusted to make contact with the surface of the sample. This may be accomplished by making contact of the actual needle point with its image reflected by the surface of the sample from a properly placed source of light. Either the reading of the dial shall then be noted or the needle brought to zero. The needle is then released for the specified period of time, after which the penetration machine is adjusted to measure the distance penetrated.

At least three tests shall be made at points on the surface of the sample not less than 1 cm. (3/8 in.) from the side of the container and not less than 1 cm. (3/8 in.) apart. After each test the sample and transfer dish shall be returned to the water bath and the needle shall be carefully wiped toward its point with a clean, dry cloth to remove all adhering bitumen. The reported penetration shall be the average of at least three tests whose values shall not differ more than four points between maximum and minimum.

When desirable to vary the temperature, time and weight, and, in order to provide for a uniform method of reporting results when variations are made, the samples shall be melted and cooled in air as above directed. They shall then be immersed in water or brine, as the case may require, for one hour at the temperature desired. The following combinations are suggested:

At 0° C. (32° F.) 200-g. weight, 60 seconds.

At 46° C. (115° F.) 50-g. weight, 5 seconds.

New Cement Plants.

The opening of a new cement plant nowadays, when the country is so well dotted with plants, is an event of importance, and the fact that two new ones have begun operations is of considerable interest. Both of them are in the Middle West, one at its extreme north, at New Duluth, Minn., the other at its extreme south, at Houston, Tex. The location of both was influenced more largely by commercial considerations than by the proximity of raw materials. The plant at New Duluth, a mill of the Universal Portland Cement Co., utilizes limestone brought by boat from the shore of Lake Huron near Alpena, Mich., and slag from the blast furnaces of the Minnesota Steel Co. at New Duluth. The plant at Houston is mill No. 2 of the Texas Portland Cement Co. It manufactures cement from oyster shells dredged from a reef in Galveston Bay and clay from Harrisburg, Tex. This plant is on tidewater, and efforts will be made to establish for it an export trade with South America.

¹This requirement is fulfilled by the American Can Co.'s Gill style oilment box, deep pattern, 3 oz. capacity.

²Journal of Agricultural Research, Vol. V, No. 24, pp. 1123-1126.

SOME NOTES ON THE DESIGN OF SULPHURIC ACID PLANTS.

An interesting discussion of acid plant design was given by Mr. S. J. Martenet, Chemical Engineer, Baltimore, Md., in a recent issue of *The American Fertilizer*. His article follows:

The ultimate object in the construction of any manufacturing plant is to produce the manufactured product so as to make the greatest possible profit; therefore the best design for a sulphuric acid plant is one that will produce sulphuric acid at the lowest possible cost per ton. The amount of acid made per cubic foot of chamber space, the per cent of nitrate of soda used, the repair and depreciation expense, the first cost of the plant, are of no interest whatever, except in so far as they affect the cost per ton of acid produced.

Cost of Acid.—Before going into a discussion of plant design it is necessary to know all the various items of expense contributing to the cost of acid; the proportion of each to the rest; and to know which of these items are affected by design, and which are affected almost entirely by management.

A plant with a daily capacity of forty tons of fifty-degree acid, costing \$100,000, using pyrites at 11 cents per unit at the plant, nitrate of soda at \$4.50 per ton at the plant, burning the cinder to 1.50 per cent sulphur, running on 3 per cent nitrate of soda, and making a yield of 4.70 lbs. of fifty-degree acid per pound of sulphur burned, will produce acid at approximately the following cost per ton:

870 lbs. pyrites.....	\$2.30
13 lbs. nitrate of soda.....	.20
Power	.25
Labor	.45
Int. (5 per cent); taxes (1 per cent); ins. (1 per cent) ..	.50
Repairs and depreciation (7½ per cent)	.54

Total cost per ton.....\$4.42

These costs are based on conditions existing in normal times and do not include interest and insurance on stock, which has no bearing on the present discussion.

Yield.—The largest item of expense is that due to the cost of pyrites; consequently, it is necessary to good design that the plant make all the acid possible, per ton of pyrite consumed. As a matter of fact the design of a plant has practically nothing to do with the amount of acid produced per pound of sulphur, except in the method of putting nitrate of soda into the system. The yield of acid per pound of sulphur is practically entirely a matter of plant management.

Nitrate of Soda.—The cost per ton of acid due to the consumption of nitrate of soda is partly influenced by design, but only to a very limited extent, except in the design of the towers and niter potting arrangements. The percentage of niter consumed is a variable quantity for any one plant, depending mostly on the management of the process, and the amount of chamber space allowed per pound of sulphur burned.

Power.—The cost per ton of acid due to power is

practically uninfluenced by design. This power is used almost entirely for compressing air and pumping water. All designs make provision for efficient air compressors and pumps. Important losses of power, however, are often caused by improper management and poor maintenance. The majority of pumps in operation are consuming from two to four times the power necessary for their operation because of bad condition of valves and cylinders.

Labor.—Labor costs are almost entirely a matter of plant management. The only effect of design possible is the installation of labor-saving devices in the burner room. Aside from this minor detail, labor costs are entirely controlled by management and are uninfluenced by design.

Overhead and Depreciation.—From the above it is readily seen that the only item of cost appreciably affected by design are the overhead costs, composed of interest on first cost, taxes and insurance; and the repair and depreciation cost. As these two items of expense constitute about 27 per cent of the total cost per ton of acid produced, the question of design remains a very important one. Therefore, the ultimate object of good design is to produce acid with the lowest possible cost due to the overhead, and repair and depreciation expense. These two items must be considered together, a fact which discloses the fault in many designs.

In the last few years all the attention of the trade seems to have been directed towards low chamber space. This means only a low first cost of plant and a consequent lower cost due to overhead. If this can be accomplished without an increase in the other items of expense a gain in economy has been secured.

Repair and depreciation costs vary in different plants from 5 per cent to 15 per cent or even more.

Let us take the plant used above as an example. Suppose the plant had been designed to operate on a lower chamber space, and that the first cost had been reduced in this way to 10 per cent, making the plant cost \$90,000. If all the other factors entering into the cost of acid remain unchanged, the cost per ton of acid would be lowered 5 cents. If this difference in design increases the repair and depreciation expense from 7½ per cent to 10 per cent of first cost, it has increased the cost of acid due to this item 11 cents per ton; a net increase in cost of 6 cents. If the repair and depreciation expense should increase to 12 per cent, the net increase in the cost of acid would be 24 cents per ton.

There is another side to this question; one almost always overlooked. A well-designed plant, properly operated, should run at least eight years without a shut-down for repairs. It is universally admitted that a shut-down is damaging to the plant, and often damaging to a great degree. In addition to this damage the shut-down entirely stops production, while all the expenses other than cost of material continue. If your

plant is forced to shut down twice in the first eight years this loss is doubled.

The important thing then in acid plant design is to consider the cost of acid due to the combined first cost of plant and repair and depreciation expense.

Phenol Producers in the United States.

According to the Weekly Drug Markets, 19 American concerns are now engaged in the manufacture of carbolic acid and turn out an estimated total of 12,000 tons per year. The following is a list of the phenol producers:

Butterworth Judson Company, and American Synthetic Company, Newark, N. J.

Semet-Solvay Company, Syracuse and Split Rock, N. Y.

Dow Chemical Company, Midland, Mich.

Aetna Explosives Company, Emporium, Pa., and Drummondville, Quebec.

New England Manufacturing Company, the Merrimac Chemical Company, Boston, Mass.

National Synthetic Company, Perth Amboy, N. J.

Barrett Company, Philadelphia, Pa.

United Gas Improvement Company, Philadelphia, Pa.

United States Standard Chemical Works, Bound Brook, N. J.

Thomas Edison, Inc., Orange, N. J.

British-American Chemical Co., Pittsburgh, Pa.

Bayer Company, Albany, N. Y.

Stillwell Chemical Company, Irvington, N. J.

Carbolite Chemical Company, Ridgefield Park, N. J.

Pittsburgh Coal Products Company, Pittsburgh, Pa.

General Coal Products Company, Monaca, Pa.

Niedlich Process Company, Milford, N. J.

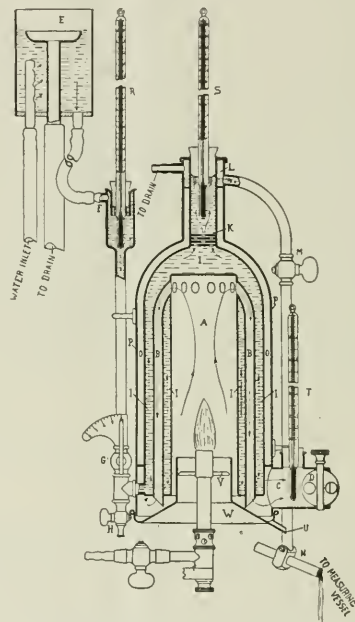
Middlesex Chemical Company, Middlesex, Conn.

The future of carbolic acid manufacture is thus outlined by Weekly Drug Markets:

"The hope for the industry is the development of other advanced products than picric acid to which phenol is a parent substance. The large concerns will probably turn over their plants to the manufacture of a few dyestuffs on a large scale, while the smaller concerns will develop along the lines of the manufacture from phenol to salicylic acid and its derivatives, their smaller production of parent substance naturally leading to consideration of the more highly advanced and more costly products. Some of these manufacturers of salicylic acid will turn their plants over to aspirin and allied antipyretics, while some will be used for methyl salicylate and synthetic flavorings. Others will market their salicylic acid to dyestuff manufacturers or will themselves embark in the manufacture of certain azo colors for which salicylic acid, by reason of its residual phenolic character, is adapted. In the list given the British-American Chemical Company has gone into the manufacture of salicylates and aspirin, and the Bayer Company, of Albany, is doing the same.

SMALL SIZE GAS CALORIMETER.

A new gas calorimeter differing in several respects from other instruments has been placed in the market by Wm. Gaertner & Co., 5349 Lake Park Ave., Chicago, Ill. The calorimeter is of the Junker type and is considerably smaller than the standard instrument. Careful tests made in the Armour Institute of Technology have shown that it is equal in accuracy to any of the standard calorimeters. A further advantage of the calorimeter is that it is mounted on a single rod which may be screwed in the base plate which is secured in the table. This gives a very solid support, allows more



Cross-Sectional View of Gas Calorimeter.

room on the table and permits adjustment to different heights.

The accompanying illustration shows a cross-section of the calorimeter. The parts of the instrument are indicated by the following letters: A, combustion chamber; B, condenser tubes; C, outlet for exhaust; D, damper for exhaust; E, inlet overflow weir; F, water inlet; G, inlet water valve; H, drain cock; I, water space; K, mixing device; L, outlet overflowing weir; M, shut off cock; N, change over device; O, air space; P, outer casing; R, inlet water thermometer; S, outlet water thermometer; T, exhaust thermometer; U, condensate drain; V, centering device for burner; W, detachable exhaust chamber.

METHODS FOR RECLAIMING WASTE SULPHITE LIQUOR.*

By JAMES BEVERIDGE.†

Of the waste products of the chemical industry few have offered so many difficulties for their utilization as the spent liquor in the manufacture of sulphite cellulose from wood, owing chiefly to the fact that the organic compounds contained in these liquors and derived from the wood vary greatly in character and are difficult to separate one from the other. According to Professor Klason dry spruce wood, which forms the principal raw fibrous material for cellulose manufacture, contains substantially 53 per cent of cellulose, 29 per cent lignin, 14 per cent of other carbohydrates, 3.3 per cent resin and closely allied bodies, and 0.7 per cent proteins. When therefore this wood is treated by the sulphite process 47 per cent of its organic matter is rendered soluble and removed in the liquor, whilst 53 per cent remains behind as cellulose.

The sulphite process as we know it today was invented by the late B. C. Tilghmann, of Philadelphia, in 1866, and consists in digesting the wood at high temperatures in aqueous solutions of bisulphites, preferably those of the lime, magnesia or soda. Either of these bases may be used, or a mixture of them employed in varying proportions. When soda is preferred as the base, it is best used alone. The greater part of the soluble constituents of the wood combine with the normal sulphites present and pass completely into solution. The chemical reactions taking place within the digester during the boiling operation have not yet been clearly defined, but enough is known at the present time from the investigations of Klein and others to indicate that certain valuable products are formed which are worth recovering commercially.

There are two well defined systems of manufacturing sulphite wood cellulose, alike in principle but differing as to the conditions under which the chemical action is carried out, namely, the Mitscherlich or "slow cook" system and the Ritter-Kellner or "quick cook" system. In the Mitscherlich system, the boiling is carried out at a temperature not exceeding 120° C. in order primarily to preserve the strength of the cellulose fiber. On the other hand, in the Ritter-Kellner or "quick cook" system the temperature of boiling may be as high as 155° C., which hastens the chemical action, but in so doing, the fiber is tendered or rendered soft. What influence the manufacturing conditions governing these two systems have upon the organic products formed has never so far as I know been investigated, but one might reasonably infer that temperature—other things being equal—would affect the result. The freshly prepared lyes from both systems possess a pungent somewhat sweetish odor, due respectively to the presence of small quantities of sulphurous acid and saccharine matter or so called

sugars. That from the Mitscherlich system is generally clear and of a bright yellow color and contains sugars varying in amount from 0.47 per cent to 1.56 per cent while that from the Ritter-Kellner system is usually turbid and dark brown with sugar contents varying from 0.89 to 2.02 per cent (Krause). One would infer from these figures that the higher temperatures promote the formation of sugars, but a further study of the most favorable conditions for their formation would prove of great value. These sugars are most important as they form the basis of the manufacture of alcohol from waste sulphite liquors.

According to the analysis of Wichelhaus these liquors obtained from spruce and bisulphite of lime have the following composition: Dry residue 82.8235 Gm. per litre (organic matter 68.344, inorganic 14.491) containing SO₂ 3.434 Gm. SO₂ combined 5.842, SO₂ free 2.560, Cl 0.024, SiO₂ 0.0024, Fe₂O₃ and Al₂O₃ 0.0102, CaO 7.176, MgO 0.004, alkalis 0.0192 Gm. per litre. The specific gravity is 1.0390.

Practically all the lime present in these liquors combines either with the sulphuric acid or with the organic matter. The same holds good whether the base be soda or other alkali, or magnesia. Of the organic compounds the most important are those that form insoluble compounds with gelatin or hide and can in consequence be used for tanning, and the fermentable sugars which may be converted into alcohol. Beyond these two the nature and amount of the others offers a somewhat limited field at the moment for exploitation as commercial products.

The following suggestions have been made for the disposal of the liquor by itself, that is, without subjecting it to chemical treatment beyond that of neutralizing the free sulphur dioxide. Its use has been suggested for laying the dust on roads; as a cementing or binding material with or without such agents as calcium sulphate, in the manufacture of briquettes from sawdust and coal; for the preservation of timber, mixed with other materials such as zinc chloride; as an artificial manure when mixed with finely ground Thomas-slag; as a source of wood pitch when evaporated to a high density and finally dried on a steam drum; as a binding material for the sand in foundries, and as a mordant in dyeing certain textile fabrics. In the early days of the manufacture it was applied as a cheap sizing material for jute and such coarse fabrics, but failed in this and in other directions on account of its strong odor and of the fact that it is slightly hygroscopic. When exposed to moist air it is apt to undergo decomposition with unpleasant results, sulphuretted hydrogen being evolved.

As regards chemical treatment, V. B. Drewsen was the first to suggest the regeneration of the liquor for refuse. He treated the liquor with lime in closed vessels and then treated the precipitate with sulphurous acid. The bisulphites formed were removed from the organic matter by filtration. Mitscherlich, who was the first to recognize the commercial importance of

*From the Journal of the Society of Chemical Industry.

†Chatham, N. B.

the tannins in the liquors, precipitated the tannins with gelatin prepared from horn, preferably in weak acid solution. The gelatin may with advantage be mixed with resin, and both dissolved in caustic or carbonated alkalis. The precipitated gelatinous mass obtained was recommended as a sizing material in the manufacture of paper, but owing to its very dark color its application was limited.

C. D. Ekman, seeking a somewhat similar result, added zinc carbonate or oxide, or produced these in the liquor itself by precipitation of a zinc salt. Later he prepared a compound which he called "dextrone" by treating the liquors obtained by his own process (involving the use of magnesium bisulphite) with either the sulphates of magnesia, soda, or potash or the corresponding chlorides, whereby a gelatinous mass separates which, when mixed with gelatin and finally dissolved in sodium bisulphite, yields a size and mordant suitable for certain branches of the textile trade.

Opl obtains a product distinguished for great adhesive properties by adding 3 to 5 per cent of a 40 per cent formaldehyde solution to the lye previous to evaporating it. Goldschmidt treats the liquor with 1 per cent of benzoyl chloride in a weak alkaline solution. The carbohydrates, tannins, and other bodies separate out and by washing and subsequent drying can be obtained as a white powder which it is said is an excellent food for poultry.

The liquor has also been recommended for use in indigo dyeing and printing owing to its reducing properties, and Phelps has prepared by a nitration process a yellow organic coloring matter which is said to be fast towards sunlight and other atmospheric influences. More recently its application to the preparation of organic dyestuffs has been confirmed by American chemists, but it remains to be seen whether or not these dyes will take their place as permanent factors in the dyeing industry.

Whatever may be thought of these chemical methods they have not been adopted to any extent, and the bulk of them have not gone beyond the experimental stage. Many of them are too costly to be of commercial value. Besides, any process or combination of processes that does not provide for the disposal of the liquor as a whole is unsatisfactory. This aspect of the problem is one that appeals most to pulp manufacturers, and anyone desiring to take commercial advantage of the valuable constituents in these liquors will require to confine their attention to the recovery of one or two of the more important organic compounds, *e. g.*, the tannins and fermentable sugars, and to the recovery, for use again, of the sulphur and base, particularly when this base is soda. The problem thus stated is somewhat narrowed down but is not an easy one as the operations involved are complicated, necessitating the erection of a chemical factory alongside the pulp mill.

When the liquor is neutralized with lime and the clear liquor evaporated down in specially constructed

pans, it can be sold as a tanning agent and as such is known in the American market as "spruce liquor." The following analysis fairly represents the composition of this commodity, and for purposes of comparison the analysis of an extract made from hemlock wood by the sulphite process and one from hemlock bark are also given.

ANALYSES OF EXTRACTS.

	Spruce sulphite process.	Hemlock wood sulphite process.	Hemlock bark extracted by water only.
	Pct.	Pct.	Pct.
Moisture	41.34	47.93	51.21
Total solids	58.68	52.07	48.76
Soluble do	58.61	51.93	41.93
Insolubles	.07	.14	3.83
Non-tannins	39.36	24.84	16.63
Tannins	19.25	27.09	25.30
Specific gravity	1.290	1.269	1.215

If we calculate the amount of tannin on 100 parts of total solids in these analyses we get respectively (in the order given) 32.80, 52.02, and 55.20 per cent. One-third of the total organic matter in the "spruce liquor" has therefore the property of combining with gelatin and hence this "spruce liquor," in conjunction with other tanning materials, such as quebracho, valonia, hemlock, etc., is being used for the preparation of certain kinds of leather, and notwithstanding a prejudice attending its use its consumption seems to be increasing. The fact that this tannin is associated with other organic compounds in combination with lime and sulphurous acid and that these have a tendency to foul the tan liquors in the pits, and perhaps enter into the composition of the leather itself, have operated against its extended use. Mitscherlich succeeded in separating these tans for the most part from the other organic matter osmosis, without having resort to precipitation methods. Opl, on the other hand, separated them by precipitation with aluminium sulphate or alum, while Kempe used the sulphates of the heavy metals. Kumpfmüller's process is stated to be more important. The liquor is heated to precipitate calcium sulphite, while the remainder of the combined lime is removed by addition of an organic acid (lactic acid). The lactic acid is harmless in the tan pits. A modification of this process consists in heating the liquor under vacuum to remove free sulphur dioxide and to precipitate calcium sulphite, then oxidizing with ozone, and finally precipitating with freshly prepared barium carbonate.

The separation of the tannins in a commercial way from the other organic bodies, more particularly the fermentable sugars, still remains unsolved. Obviously if this can be accomplished, either by precipitation or otherwise and the sugars left untouched, the most valuable organic constituents of the lye can be utilized. The sugars can be converted by fermentation into alcohol and recovered. This process is one of the most interesting that has been introduced to manufacturers in recent years, and although simple in principle, yet it is attended with difficulties of a technical character requiring a high state of scientific knowl-

edge for their solution. The names of Wallin and Ekström are intimately connected with the origin and development of this process. The hot lyes from the pulp digester are deprived of the free sulphur dioxide by addition of lime or by boiling *in vacuo* or otherwise, the resulting calcium sulphite or sulphur dioxide being recovered and sent back to the acid plant of the sulphite pulp mill. The liquors are then cooled by aeration or by means of a heat economizer, the last traces of acid being removed by an alkali, preferably ammonia. It is said that the neutralization of the last traces of acid by ammonia appreciably increases the yield of alcohol. The prepared liquors are then subjected to fermentation by the aid of a specially cultivated yeast acclimatized to its particular environment in the vats. Finally the alcohol is distilled off. This, in brief outline, is the alcohol process as it is carried out today in Scandinavia.

Passing now to a consideration of the recovery of the inorganic constituents of these lyes, viz., the sulphur and lime or magnesia, so long as these alkaline earths are used as the base in the preparation of the bisulphite liquor, there seems little hope of any process of recovery being commercially successful. If, however, the lime or magnesia be replaced by soda the possibilities in this direction are greatly increased, for by simple evaporation of the lye, and calcination of the residue either with or without lime, sodium sulphide can be obtained, which in its turn may be converted into carbonate. Sodium bisulphite offers certain advantages to the pulp maker. The "cooking" operation is carried out with great ease, and the highest quality of cellulose is obtained. The waste lye moreover contains substantially no lime and hence no trouble can arise from lime precipitates.

L. J. Dorenfeldt was the first to suggest the recovery of the sulphur and soda in such lyes, by using the well known reactions of the Leblanc soda process. The lyes were evaporated to dryness, mixed with limestone or lime, and calcined to obtain ball soda. This when lixiviated yielded sodium carbonate more or less mixed with caustic soda and sulphide, and calcium sulphide as a residue. After the alkaline liquors have been freed from sodium sulphide, they are sent to the acid plant of the pulp mill for conversion into bisulphite, while the calcium sulphide may be decomposed, as in Chance's process, by carbon dioxide into calcium carbonate and free hydrogen sulphide which is oxidized. This process is, however, complicated and involves the use of extra fuel and lime in the preparation of the ball soda, and has not been adopted. Several modifications of the Leblanc process may be suggested. The ball soda may be heated under pressure, in presence of water, to obtain sodium sulphide and calcium carbonate, as in Weldon's process for the preparation of sodium sulphide. The sodium sulphide obtained may then be decomposed by carbon dioxide.

A simpler method is to add a quantity of sulphuric acid equivalent to the combined sulphur dioxide, boil

and finally evaporate to dryness, either with or without the separation of the precipitated organic matter by filtration, and calcine the mass in specially constructed furnaces to obtain sodium sulphide, which can then be decomposed with carbon dioxide. In this system the sulphuric acid decomposes the organic bodies that are combined with normal sodium sulphite, liberating sulphur dioxide, which is recovered with precipitation of organic matter (chiefly lignin). The organic matter in the dried residue evolves sufficient heat on burning to satisfy the requirements of the chemical reaction taking place within the furnace, this reaction being endothermic, and also sufficient heat to evaporate the liquors to dryness when refined systems of evaporation are employed. The decomposition of the sodium sulphide in aqueous solution by carbon dioxide presents some difficulties owing to the soda separating to a great extent as bicarbonate, but these difficulties are not insurmountable.

It will be seen that in such systems of recovery there is nothing in the reactions themselves necessitating the addition of any compound other than those required to make up the chemical and mechanical losses inevitable in such operations. The carbon dioxide, sulphur and soda are all circulating quantities.

There is yet an alternative method that has been formulated for the recovery of the soda (and sulphur if need be) by the aid of alumina, but this necessitates the manufacture of an additional product, namely, aluminum sulphate. This process consists in calcining the dried residue from the waste lye with lime and bauxite in slight excess of equivalent proportions according to the equation: $3\text{Na}_2\text{S} + 3\text{CaO} + \text{Al}_2(\text{OH})_6 = \text{Al}_2(\text{ONa})_6 + 3\text{CaS} + 3\text{H}_2\text{O}$. The calcined mass is lixiviated with water, sodium aluminate passing into solution, while the calcium sulphide remains behind as an insoluble residue and contains all the iron originally present in the bauxite. If desired this residue may be treated for recovery of the sulphur. By passing sulphur dioxide into the hot solution of sodium aluminate, the alumina separates out as a dense granular precipitate in the form of hydroxide, sodium sulphite being at the same time formed. The aluminum hydroxide is separated in a filter press, washed to remove sodium sulphite, and finally dissolved in a sulphuric acid. The aluminum sulphate thus obtained is entirely free from iron and can command the highest price in the market for such salts. The sodium sulphite is passed over to the pulp mill for conversion into bisulphite for reuse.

In conclusion this problem of completely working up and utilizing the more important compounds contained in these lyes is not so difficult of solution, but it involves the adoption by sulphite pulp manufacturers of a series of chemical operations which, although well defined in character, yet necessitate the investment of additional capital in plant and machinery, and perhaps the manufacture of some additional products other than those named.

OPIMUM ASSAY: COMPARISON OF THE METHODS OF THE UNITED STATES AND BRITISH PHARMACO- POEIAS.*

By CARL E. SMITH.†

It will be generally conceded that no method for the quantitative determination of morphine in opium has yet been published that is capable of the degree of accuracy highly desirable in a medium that serves as a basis for price adjustments of a drug as costly as opium. The assay methods of the pharmacopoeias have been arranged and adapted primarily for the adjustment of doses, for which purpose they are reliable enough, with few exceptions. A fair degree of accuracy is all that can be expected in their application, since editors of pharmacopoeias take the stand that pharmacopoeial methods of testing should be simple enough to be used successfully by pharmacists having only limited practice and training in analysis. But simplification of analytical procedures often entails a sacrifice in precision of results, and this is particularly true of opium assays. Buyers and sellers of large quantities of opium, therefore, do not generally rely upon pharmacopoeial assay methods to ascertain as closely as possible the morphine contents of this drug.

The method of the British Pharmacopoeia of 1914 may be expected to have the same limitations as others of its kind. Nevertheless, it is of interest because it is one of the latest in this field having official sanction and, therefore, may be expected to embody, to some extent, such advances as have been made in recent years in this branch of analysis. In its present form it has not been in use long enough for many data concerning it to have accumulated, and the writer has not yet seen any reports of critical study that furnish a clue as to the degree of accuracy of which it is capable. Such data would be useful, also, in view of the prevailing differences of opinion in this country about the relative merits of lime methods, of which the British is an example, and methods of the type originated by the late Dr. E. R. Squibb, as adopted by the U. S. P. in the seventh and eighth revisions.

The process of the eighth revision was held by Dr. Squibb to yield results a little too low, as he was able to obtain in actual manufacture somewhat larger yields of morphine than assays of the opium by that method indicated it to contain. It should be considered, however, that when Dr. Squibb made that statement medicinal morphine and its compounds contained notable proportions of unsuspected impurities that would not now be tolerated and which appreciably increased manufacturing yields. Dr. A. R. L. Dobne¹ considers the U. S. P. method to give *much too low* results. A manufacturer of opium alkaloids, who bases his conclusion on manufacturing yields by up-to-date

methods, has stated to the present writer his conviction that the process gives *too high* results. These are only a few examples of the many differences of view that tend to throw doubt upon the reliability of the U. S. P. method.

The B. P. method, not being accessible to many American readers as yet, is copied here in full:

OPIMUM ASSAY METHOD OF THE BRITISH PHARMACOPOEIA OF 1914.
Opium, in No. 50 powder, dried at 60°..... 8 grammes
Calcium Hydroxide, freshly prepared..... 2 grammes
Ammonium Chloride..... 2 grammes
Alcohol (90 per cent)..... } of each a sufficient quantity
Ether..... }
Distilled Water..... }

Triturate together the Opium, calcium hydroxide, and 20 millilitres of water, in a mortar until a uniform mixture results; add 60 millilitres of water and stir occasionally during half an hour. To 51 millilitres of the filtered liquid (representing 5 grammes of Opium) in a convenient vessel add 5 millilitres of alcohol (90 per cent), and 25 millilitres of ether; shake the mixture; add the ammonium chloride, shake well and frequently during half an hour; set aside for 12 hours for the morphine to separate. Counterbalance two small filters; place one within the other in a small funnel in such a way that the triple fold of the inner filter shall be superposed upon the single fold of the outer filter; wet them with ether; remove the ethereal layer of the liquid in the vessel as completely as possible by means of a small pipette, transferring the liquid to the filter; rinse the vessel with 10 millilitres of ether, again transferring the ethereal layer, by means of the pipette, to the filter; wash the filter with a total of 5 millilitres of ether, added slowly and in portions. Let the filter dry in the air and pour upon it the contents of the vessel in portions, in such a way as to transfer the granular crystalline morphine as completely as possible to the filter. When all the liquid has passed through, wash the remainder of the morphine from the vessel with morphinated water until the whole has been removed. Wash the crystals with morphinated water until the washings are free from color, allow the filter to drain, and dry it, first at 60° and finally, for two hours, at 115°. Weigh the crystals in the inner filter, counterbalancing by the outer filter. Dissolve 0.2 gramme of the crystals in 10 millilitres of N/10 solution of sulphuric acid, and titrate back with N/10 solution of sodium hydroxide, solution of methyl orange being used as indicator. Each millilitre of the acid neutralized by the alkaloid corresponds to 0.0285 gramme of pure anhydrous morphine. The weight of pure anhydrous morphine obtained, as indicated by the titration, plus 0.051 gramme, the average loss of morphine during the process, together amount to 0.5 gramme, representing in 100 grammes of the dry powdered Opium 10 grammes of morphine, calculated as anhydrous. Limit of error 0.5 gramme in excess or defect.

Morphinated Water, prepared by digesting pure Morphine in Chloroform Water for seven days at a temperature of 15.5°, shaking occasionally so as to obtain a saturated solution of the alkaloid, and filtering from the undissolved morphine.

COMPARATIVE ASSAYS.

The assays given below are of a specimen of powdered opium bearing the label of Merck & Co., and stated to contain the U. S. P. percentage of morphine.

To facilitate comparison, the results in this paper are in all cases stated as hydrated morphine.

PER CENT OF MORPHINE FOUND.		
U.S.P., 8th Rev.	B.P., 1914.	
12.19	12.37	
12.10	12.48	
12.23	12.33	
12.21	12.34	
Mean result....	12.18	12.38

*From the July American Journal of Pharmacy.
†Carl E. Smith Testing and Research Laboratory, 5 Beekman St., New York City.
¹Jour. Am. Phar. Ass. 1915, vol. 4, p. 85.

It is seen that with this particular sample no marked differences in results were obtained by the two methods, though a tendency toward somewhat higher figures are shown by the B. P. method. But it would not be safe to conclude that a similar concordance of results by the two methods would be obtained, or that the British process would consistently give a little higher results with any and all kinds of opium of abnormal composition. The methods differ radically in their means of arriving at the end, and opium from different sources varies much in the proportions of constituents that contaminate the precipitated alkaloid and probably, to some extent, affect its solubility in the precipitate liquors.

The U. S. P. assumes that those impurities in the morphine which are not excluded by the lime water correction compensate with sufficient accuracy for the loss of morphine in the precipitate liquors. The proportion of such impurities, however, is subject to a wide variation. In a considerable number of assays of various kinds of opium by the U. S. P. method the writer has found in the morphine, besides matter insoluble in lime water, from 5 to 11 per cent of other impurities—much too great variation to be counterbalanced with any degree of certainty by the loss of morphine in liquors.

Attention should be called here to the rather vague directions in the U. S. P. pertaining to washing the crystals on the filter with the alcohol solution of morphine. It is important, though not stated, that washing with this solution be continued until the washings are practically colorless. This requires 10 cc. or more. Failure to do this may cause the crystals to retain a much larger quantity of alcohol-soluble impurities than is allowable. Some years ago the writer was asked to investigate the causes of discrepancies in assays of a number of lots of opium, when the analyst representing one side persistently obtained higher figures than the other side. The differences were found to be due to nothing else than insufficient washing with the alcohol solution of morphine. The procedure of washing as here advocated was used in the laboratories of the late Dr. E. R. Squibb when the writer was in his employ and made many such assays.

In the B. P. it has been sought to overcome the variable error due to impurities in the morphine by an attempt to determine the actual morphine in the crude crystals by titration with acid and by adding to the quantity so found the quantity assumed to remain in the precipitate liquors. The same procedure has sometimes been proposed for use with the U. S. P. method. With lime methods this is doubtless a nearer approach to accuracy, though sources of error still remain. With the U. S. P. method this plan is liable to lead to much too high results.

Manufacturers of opium alkaloids have long known the difficulty of separating codeine from morphine by means of ordinary processes of crystallization and precipitation, and morphine compounds of the mar-

ket commonly contain this alkaloid; up to a few years ago it was not unusual to find 5 per cent or more. But the fact that morphine separated from opium under the conditions of the assay methods now under discussion may contain up to 3 per cent of its weight of ether- and chloroform-soluble alkaloid, chiefly codeine, seems to have escaped general notice, so far as the literature on opium assay is evidence. Codeine, being a strong base, is consequently included as morphine in titrations of the crude alkaloid. Even after a second precipitation from a lime solution containing alcohol, in the "Mallinckrodt Re-assay," the writer has invariably found in morphine from all types of precipitation processes from 1 to 2 per cent of codeine, whenever he has looked for it. In view of the ready solubility of free codeine in all of the liquids used in both of the processes being discussed, this might well be doubted by those who have not proved it for themselves. That is easily done, however, by dissolving the twice-precipitated morphine in fixed alkali solution and shaking out with ether. The residue remaining after evaporation of the ether will usually yield the codeine pure enough for identification by means of the customary color reactions and the melting point.

In the morphine from the comparative assays by the B. P. method, reported above, other alkaloids were found equivalent to 2.31 per cent of its weight of codeine, as determined by titration of the extract obtained with immiscible solvent; in that from each of two pairs of assays by the U. S. P. method, 2.21 and 2.34 per cent, respectively, were found. It will be seen that the discrepancy caused by including this in the titration as morphine cannot be ignored when the highest possible degree of accuracy is desired.

Another source of variable error, also additive in its effect, is often overlooked by those advocating titration of morphine obtained by either of the two types of methods. Lime methods cause contamination of morphine with varying quantities of matter insoluble in both alcohol and lime water, and these often neutralize enough acid to introduce an appreciable error in the titration. The alkalinity of these substances is, at least in part, due to presence of calcium carbonate, which cannot be entirely excluded because of the nature of the method. Morphine from U. S. P. assays sometimes contains more than 10 per cent of its weight of matter insoluble in alcohol or lime water, of which calcium ammonium meconate forms a large proportion. It is well known that this insoluble matter may neutralize much mineral acid under the ordinary conditions of alkaloid titration. If, therefore, the B. P. procedure of titrating the crude morphine be applied to the U. S. P. method, the final results will in many cases be very much too high.

An example will illustrate the effect of only a small quantity of such insoluble impurities, also that of an average amount of chloroform-soluble alkaloid.

The sample of opium reported upon above yielded

in one case 12.49 per cent of crude morphine by the U. S. P. method. The lime-water correction applied to a portion of this gave 12.21 per cent as the final result by that method. Another portion was dissolved in N/10 acid and titrated back with N/20 alkali, with methyl red as indicator. Another portion was boiled with alcohol and the insoluble matter filtered out and washed until the washings were free from alkaloid. This insoluble matter was also titrated. The alcohol solution and washings were evaporated to dryness, the residue dissolved in caustic soda solution and shaken out with chloroform. The filtered chloroform solutions were evaporated to dryness and the residue titrated. The results were as follows:

1.249 Gm. of crude morphine.....	N/10 acid required. 46.39 Cc.
Alcohol insoluble matter in it.....	1.11 Cc.
Chloroform soluble matter in it.....	0.87 Cc.
	1.98 Cc.
Actual morphine in it (so far as known).....	38.41 Cc.
38.4 Cc. of N/10 acid represent.....	1.156 Gm. of morphine
Additive correction for solubility of morphine in precipitate liquors....	0.056 Gm.

1.212 Gm., or 12.12 per cent of morphine.

Had the correction for other alkaline substances in the crude morphine been omitted, the result by titration would have been 12.72 per cent, obviously too high. That the U. S. P. (Squibb) method may give results that agree closely with those arrived at with this more complicated procedure is also shown by this example, but data are at hand indicating that this may be rather an exception. Two samples of "gum" opium (sources unknown) gave distinctly higher results by the official method, and in triplicate tests of one of them there was also a greater variation in the result than when corrections for impurities and solubility were made. These differences are shown below.

Opium.	Per cent morphine.	
	U.S.P. method.	U.S.P. method corrected.
(1)	11.40	11.01
(2)	14.91	14.44
	14.68	14.35
	14.79	14.37

It is difficult to escape the conclusion that the U. S. P. method with lime-water correction only has a tendency of giving somewhat too high figures.

The solubility figure used above was determined as follows: One gramme of fully hydrated morphine, free from uncombined moisture and chloroform-soluble alkaloids, was dissolved in a moderate excess of dilute sulphuric acid. The solution was diluted with water to 20 Gm., then subjected to the U. S. P. procedure for precipitation of morphine. After standing over night at room temperature (during hot weather) the mixture was kept at 15° to 16° for three hours, the morphine then filtered out, washed and dried as usual. The loss, which scarcely differed in duplicate determinations, was 0.056 Gm.

It is not a simple matter to determine accurately the small quantity of morphine remaining in assay liquors,

which is mixed with a much larger quantity of other alkaloids and other interfering materials. The few attempts so far made by the writer, as time permitted, by means of ether, iso-butyl alcohol and chloroform mixture, etc., gave results far from convincing, and for that reason these are not included in this report. The figure obtained with pure morphine is probably only slightly lower than the quantity of morphine lost in actual assays, provided the necessary conditions for obtaining a maximum precipitation are strictly adhered to, particularly in regard to sufficient agitation, time allowance, and low temperature. Moreover, it is quite possible that any small deficiency in this solubility figure may be counterbalanced by small quantities of alkaline impurities in the morphine that have not been discovered and, therefore, are not allowed for.

The B. P. assays given in this paper were also checked by a correction for alkalinity of substances soluble in chloroform and insoluble in alcohol. In comparison with the same procedure applied to the U. S. P. assays of the same sample the following differences are shown:

	U. S. P.	B. P.
Official method	12.21 per cent.	12.38 per cent.
Corrected	12.12 per cent.	11.96 per cent.

Although corroboration of the data presented in this paper by comparative tests of all kinds of opium are very desirable, there is enough evidence to warrant at least the tentative inference that both the U. S. P. and the B. P. method have a tendency toward somewhat too high results, but that neither method is liable to give results very far from the truth.

For rapid approximate results the writer favors lime methods and methods of the type adopted by the German Pharmacopoeia of 1910, as they are expeditious and require comparatively little labor, but for the highest degree of precision possible under the present conditions of incomplete knowledge he would recommend the Squibb method as given in full detail in *Ephemeris*, vol. 3, p. 1150, and in the United States Dispensatory, nineteenth edition, with omission of the lime-water correction and substitution for it of titration of the morphine, corrections to be made for alkaline impurities and for solubility. Several variations in procedure being possible, the following is proposed as the simplest:

CORRECTION FOR U. S. P. (SQUIBB) METHOD OF OPIUM ASSAY.

Mix thoroughly the weighed crude morphine from 10 Gm. of opium and divide it in two equal portions. Boil one portion in a 100-cc. flask with about 50 Cc. of neutral (preferably absolute) alcohol, reserving the other for a duplicate determination or for use in case of accident. Continue heating until there is no further visible diminution of undissolved residue. Filter out insoluble matter and wash it with hot alcohol until the washings are free from alkaloid. Dilute the filtrate and washings with an equal volume of distilled water that has been rendered neutral to methyl

red, if necessary, and titrate the solution with N/10 acid, using methyl red as indicator. Evaporate the alcohol from the titrated solution below a boiling temperature, add fixed caustic alkali solution moderately in excess of the quantity required to convert the morphine into alkali morphinate, and shake it out with three 10-cc. portions of chloroform. Filter the chloroform extracts successively through a small, dry filter, wash the filter with chloroform, and evaporate filtrate and washings to dryness. Determine the volume of N/10 acid required to neutralize the extracted matter and subtract it from the volume required for the first titration. The remainder, multiplied by 2, gives the volume of N/10 acid representing the morphine in the crude alkaloid from 10 Gm. of opium. To the weight of hydrated morphine so found add 0.056 Gm. The sum, multiplied by 10, gives the percentage of hydrated morphine in the opium.

The volumetric solutions should be standardized with pure morphine and the titrations for that purpose performed in the same way as in actual determinations.

The procedure advocated above is applicable also to lime and other precipitation methods, with a suitable readjustment of the solubility figure.

The writer agrees with Dr. Dohme² that shaking-out methods are likely in the future to supplant precipitation methods of opium assay, but he also concurs in the view of Dr. A. B. Lyons³ that these newer methods still require a thorough trying-out to establish their reliability and their superiority over those generally accepted. In trial of possible shaking-out methods one is struck with the great tedium attending complete removal of other alkaloids before shaking out the morphine, and the difficulty of obtaining a precise end-point in titrations because of the presence of much color and substances that not only obscure the color changes of indicators, but also impair their sensitiveness. If authors of such processes would publish them in complete detail, it is possible that others might be able to obtain with them such satisfactory results as they do. As it is, each person trying them must waste considerable time in working out the details himself.

SUMMARY.

The conclusion which requires confirmation with opium of abnormal composition, has been reached that the U. S. P. and B. P. methods give fairly accurate results, with a tendency toward somewhat too high results.

A method of double titration is proposed, by means of which a nearer approach to accuracy may be attained through elimination of sources of variable error due to presence of alkaline substances other than morphine in the crude morphine obtained in precipitation methods.

A solubility correction figure has been determined

for the U. S. P. (Squibb) method and is proposed for use in conjunction with the double titration.

FERTILIZER INDUSTRY OF THE UNITED STATES.

The quinquennial census of American manufacturing industries, taken in 1914, has revealed in some cases notable advances in production as compared with the output of 1909. Few industries, however, can equal in this respect the manufacture of fertilizers. In the course of five years it has increased its output in quantity by 49.8 per cent; in value, by 50.5 per cent. The number of establishments primarily devoted to this branch has grown from 550 in 1909 to 784 in 1914.

A preliminary summary of the data collected in this latest census of the American fertilizer industry has been prepared in the Bureau of the Census. The most important results are tabulated as follows:

Materials or products.	1909.	1914.
Principal materials used.		
Ammoniates:		
Tons	1,018,555	1,463,278
Cost	\$19,097,415	\$31,662,515
Cottonseed meal—		
Tons		325,234
Cost		\$8,419,383
Tankage and ammoniates not elsewhere specified.....	842,557	
Cost	\$17,200,611	
Fish—		
Tons	242,145	250,110
Cost	\$4,066,613	\$3,111,991
Ammonium sulphate:		
Tons	65,590	149,924
Cost	\$3,732,016	\$9,015,163
Cyanamid or lime nitrogen:		
Tons	*	25,911
Cost	*	\$1,176,119
Nitrate of soda:		
For mixed fertilizers—		
Tons		147,150
Cost		\$6,807,228
For acid manufacture.....	89,546	
Cost	\$3,916,320	
Phosphate rock:		
Tons	4,549,497	2,080,961
Cost	\$8,828,834	\$11,222,992
Bone—raw, ground, steamed, and bone discard:		
Tons	*	148,191
Cost	*	\$3,410,545
Pyrites:		
Tons	457,507	613,842
Cost	\$2,843,548	\$3,590,235
Sulphur:		
Tons	4,236	2,041
Cost	\$68,924	\$42,716
Basic slag or Thomas phosphate powder:		
Tons	*	16,190
Cost	*	\$144,213
Guano:		
Tons	*	120,128
Cost	*	\$445,416
Kainit:		
Tons	347,104	448,885
Cost	\$3,008,183	\$3,939,263
Potash salts:		
Tons	269,974	4529,973
Cost	\$7,708,544	\$12,774,113
Muriate of potash—		
Tons	*	177,372
Cost	*	\$6,497,364

²Loc. cit.

³Ibid., p. 97.

Sulphate of potash—		
Tons	*	39,232
Cost	*	\$1,684,998
Double manure salts—		
Tons	*	108,580
Cost	*	\$1,740,241
Other potash salts—		
Tons	*	187,359
Cost	*	\$2,399,277
Sulphuric acid, total consumption (amount purchased and amount made and consumed, reduced to 50° Baumé), tons	1,462,193	1,973,054
Superphosphates or acid phosphates, total consumption (amount purchased and amount made and consumed), tons.....	2,372,075	3,785,495
Products.		
Total value.....	\$511,871,481	\$568,388,405
Fertilizers:		
Tons	5,618,234	8,414,959
Value	\$100,089,971	\$152,815,786
Complete fertilizers—		
Tons	3,001,370	4,488,565
Value	\$63,104,917	\$97,046,825
Ammoniated fertilizers—		
Tons	522,389	1,116,739
Value	\$11,004,390	\$24,344,271
Superphosphates and concentrated phosphate fertilizers—		
Tons	1,494,097	1,760,290
Value	\$16,458,341	\$16,145,659
Other fertilizers—		
Tons	600,378	1,049,365
Value	\$9,522,320	\$15,279,031
Other products, value.....	\$11,781,510	\$15,572,619

The above table shows in a striking manner the present trend of the fertilizer movement. Nitrogen plays relatively a much more important role than was the case a decade ago. During the five years in question the consumption of Chile salt-peter, or sodium nitrate, has increased 81 per cent. The consumption of ammonium sulphate increased 128 per cent, and this enlarged demand was met almost entirely by the rapidly expanding output of the domestic by-product coke ovens. Cyanamid manufactured on this continent thus far only at Niagara Falls, Ontario, has become a distinct factor, and its use is steadily growing.

The consumption of potash in the form of the mineral kainit increased 29 per cent. In the use of more concentrated forms, especially the muriate, the increase was 96 per cent. In contrast with these figures stands the increase in the consumption of raw phosphate—34 per cent. The amount of basic slag employed in the fertilizer industry, 16,190 tons, is much below what would naturally be expected in a country possessing such highly developed iron and steel industries.

The geographical location of the industry is predominantly in the South, harmonizing with the notable consumption of fertilizers in that section. Of the 1,124 establishments engaged in the industry, 293 were located in Georgia, 103 in Alabama, 85 in South Carolina, 60 in North Carolina, 66 in Pennsylvania, 61 in Virginia, 50 in Maryland, 31 in Ohio, and 30 in New Jersey. Other States contain less than 30 each.

*Figures not available.

†Includes 17,430 tons, value \$452,233, not distributed by kind.

‡Includes fertilizer product, valued at \$15,192,253 in 1914 and \$7,911,268 in 1909, made by establishments engaged primarily in the manufacture of other commodities.

THE TRADE AGREEMENT OF GREAT BRITAIN AND HER ALLIES.

The trade agreement signed on June 17 by representatives of Great Britain, France, Russia, Italy, Japan, Belgium and Serbia, may have far reaching effect on industries in the United States. In fact Congress is now considering legislation to protect the markets of this country. The principal proposal under consideration is understood to be a retaliatory provision aimed to withhold American resources from any power that discriminates against the United States. In view of its possible effect on the chemical industry the text of the Paris agreement is given below:

PROVISIONS DURING WAR.

The measures provided for the remaining war period are:

I.

Laws and regulations prohibiting trading with the enemy shall be brought into accord, for this purpose:

(a) The allies will prohibit their own subjects and citizens and all persons residing in their territories from carrying on any trade with the inhabitants of enemy countries of whatever nationality, or with enemy subjects, wherever resident, persons, firms and companies whose business is controlled wholly or partially by enemy subjects or subject to enemy influence, whose names will be included in a special list.

(b) The allies will also prohibit importation into their territories of all goods originating or coming from enemy countries.

II.

Business undertakings, owned or operated by enemy subjects in the territories of the allies, are all to be sequestered or placed under control. Measures will be taken for the purpose of winding up some of these undertakings and realizing the assets, the proceeds of such realizations remaining sequestered or under control. In addition, by export prohibitions, which are necessitated by the internal situation of each of the allied countries, the allies will complete the measures already taken for the restriction of enemy supplies, both in the mother countries and the dominions, colonies, and protectorates:

1. By unifying lists of contraband and export prohibition, particularly by prohibiting the export of all commodities declared absolute or conditional contraband.

2. By making the grant of licenses to export to neutral countries, from which export to the enemy territories might take place, conditional upon the existence in such countries of control organizations approved by the allies, or in the absence of such organizations, upon special guarantees such as the limitation of the quantities to be exported, and supervision by allied consular officers, etc.

MEASURES ADOPTED FOR THE PERIOD OF THE COMMERCIAL, INDUSTRIAL, AGRICULTURAL, AND MARITIME RECONSTRUCTION OF THE ALLIED COUNTRIES.

I.

The allies declare their common determination to insure the re-establishment of the countries suffering from acts of destruction, spoliation, and unjust requisition, and they decide to join in devising means to secure the restoration to those countries, as a prior claim, of their raw materials, industrial, agricultural plant and stock, and mercantile fleet, or to assist them to re-equip themselves in these respects.

II.

Whereas, the war has put an end to all treaties of commerce between the allies and enemy powers, and it is of essential importance that during the period of economic reconstruction the liberty of none of the allies should be hampered by any claim put forward by enemy powers to most favored nation treatment, the allies agree that the benefit of this treat-

ment will not be granted to these powers during a number of years to be fixed by mutual agreement among themselves.

During this number of years the allies undertake to assure each other, so far as possible, compensatory outlets for trade in case consequences detrimental to their commerce should result from the application of the undertaking referred to in the preceding clause.

III.

The allies declare themselves agreed to conserve for the allied countries, before all others, their natural resources during the whole period of the commercial, industrial, agricultural, and maritime reconstruction, and for this purpose they undertake to establish special arrangements to facilitate the interchange of these resources.

IV.

In order to defend their commerce and industry and their agriculture and navigation against economic aggression, resulting from dumping or any other mode of unfair competition, the allies decide to fix by agreement a period of time during which commerce with the enemy powers will be submitted to special treatment and goods, originating from their countries, will be subjected either to prohibitions or to a special regime of an effective character. The allies will determine by agreement, through diplomatic channels, the special conditions to be imposed during the above mentioned period on the ships of enemy powers.

V.

The allies will devise measures to be taken jointly or severally for preventing enemy subjects from exercising in their territories certain industries or professions which concern national defense or economic independence.

PERMANENT MEASURES OF MUTUAL ASSISTANCE AND COLLABORATION AMONG THE ALLIES.

I.

The allies decide to take the necessary steps without delay to render themselves independent of enemy countries in so far as regards raw materials and manufactured articles essential to the normal development of the economic activities. These measures will be directed to assuring the independence of the allies not only so far as concerns sources of supply but also as regards their financial, commercial, and maritime organization.

The allies will adopt such measures as seem to them most suitable for the carrying out of this resolution according to the nature of the commodities and having regard to the principles which govern their economic policy. They may, for example, have recourse to either enterprises subsidized and directed or controlled by the governments themselves or to the grant of financial assistance for the encouragement of scientific and technical research and the development of national industries and resources, or to customs duties or prohibitions of a temporary or permanent character, or to a combination of these different methods.

Whatever may be the methods adopted, the object aimed at by the allies is to increase the production within their territories as a whole to a sufficient extent to enable them to maintain and develop their economic position and independence in relation to enemy countries.

II.

In order to permit the interchange of their products the allies undertake to adopt measures facilitating mutual trade relations, both by the establishment of direct and rapid land and sea transport services at low rates and by the extension and improvement of postal, telegraphic and other communications.

III.

The allies undertake to convene a meeting of technical delegates to draw up measures for the assimilation, so far as may be possible, of their laws governing patents, indications or origin and trademarks. In regard to patents, trademarks,

literary and artistic copyright, which come into existence during the war in enemy countries, the allies will adopt, so far as possible, an identical procedure to be applied as soon as hostilities cease. This procedure will be elaborated by the technical delegates of the allies.

IV.

Whereas, for the purpose of their common defense against the enemy, the allied powers have agreed to adopt a common economic policy on the lines laid down in the resolutions which have been passed, and, whereas, it is recognized that the effectiveness of this policy depends absolutely upon these resolutions being put into operation forthwith, the representatives of the allied governments undertake to recommend that their respective governments shall take, without delay, all the measures, whether temporary or permanent, requisite to giving full and complete effect to this policy forthwith, and to communicate to each other the decisions arrived at to attain the object.

FUEL VALUE OF SPENT HEMLOCK BARK.*

By BYRON E. PARKS.

There was a time, not very many years ago, when the tanner cared very little about the fuel value of spent tan bark. He had a surplus, so the efficient combustion or the relative fuel value of this refuse was of little moment. They were only concerned with the problem of how to dispose of it.

Improved leaching methods and the increased use of extracts have materially reduced the quantity of bark used per unit of leather output, so that there is no longer a surplus and it is now necessary to supplement the spent tan bark with some other fuel, usually coal. This has brought home to the tanner the fact that the spent tan, which had heretofore been considered as a refuse to be disposed of, has a distinct monetary value as fuel. Also, that the question of efficient combustion is well worthy of consideration.

What is the fuel value of spent tan bark? Or, in other words, what is the relative value of tan bark as fuel, compared to the average bituminous steam coal?

To answer this question, it is necessary to analyze the bark to determine just what portion of it is available as fuel after the leaching process.

Take one cord of average air-dried bark as a basis of calculation. It will weigh, in the condition in which it comes from the pile, about 2,240 lbs., and will carry about 15 per cent of moisture, equal to 336 lbs. The tannin content and the other matter soluble in water will amount to about 11 per cent of the weight of *absolutely dry* bark, equal, say, to 210 lbs. Assume that leaching is carried to 95 per cent efficiency, the tannin and other solubles extracted from the bark would weigh 199.5 pounds, say in round numbers 200 lbs.

Deducting the moisture content, 336 lbs., and the solubles, 200 lbs., leaves as a residue, *absolutely dry*, 1,704 lbs., or say, in round numbers, 1,700 lbs. from each cord of bark which is available as fuel.

*Paper presented at the 12th Annual Meeting of the American Leather Chemists Association, Atlantic City, N. J., June 3, 1916, and printed in the Journal of the Society.

Owing to the fact that each cord of bark, even from the same pile, will vary somewhat in its condition, the figures here given are intended to be average, rather than extremes either way.

Analyses made by a number of authorities vary to some extent as to the thermal value of spent hemlock bark, but probably no more than would be expected of samples obtained under varying conditions, and when this is taken into consideration the differences are very slight.

As long ago as 1875, Mr. Theron Skeel, a well known engineer of that time, made a series of carefully conducted experiments in burning spent hemlock bark, alone, in various types and proportions of furnaces. In connection with these experiments he obtained analyses of a number of samples of spent tan bark which run from 9,000 to 9,800 B. t. u. per pound of spent bark *absolutely dry*.

Analyses which the writer has obtained at various times have shown about the same B. t. u. value. Therefore the writer has adopted a value of 9,500 B. t. u. as a fair average for this class of fuel, for estimate purposes.

Spent hemlock bark, in the condition as usually discharged from the leach, the writer has found to average 65 per cent moisture. Therefore he uses that factor in estimating the fuel value of wet tan bark. The residue, *absolutely dry*, from 2,240 lbs. of bark ground, we have found weighs 1,700 lbs., carrying 65 per cent moisture. The gross weight would be

$$1,700 \times 100 = 4,856 \text{ lbs.}$$

.35

A pound of wet tan bark carrying 65 per cent moisture would represent only 0.35 lb. of bark *absolutely dry*. We have, then, as the thermal value of wet spent tan bark, the following:

$$9,500 \times 0.35 = 3,325 \text{ B. t. u.}$$

Now before the wet bark, as fed to the furnace, can be consumed, the moisture content must be evaporated from and at 212° , then superheated to the temperature of the escaping chimney gases, and the B. t. u. required to do this must be deducted from the fuel value of the bark as fired, in order to arrive at its net fuel value.

The average temperature of tan bark as fed to the furnace is taken at 100° F., the average temperature of escaping chimney gases at 500° F., and the specific heat of superheated steam at constant pressure 0.463. We have, then, the following:

	Heat units.
To raise the temperature of 1 lb. of water from 100° to 212° will require.....	112.82
To evaporate 1 lb. of water from and at 212° will require	970.4
To superheat 1 lb. of steam from 212° to the temperature of escaping chimney gases, assumed at 500° will require.....	133.34
Total	1,216.56
$1,216.56 \times 0.65 = 790.76$ heat units.	

This would then represent the B. t. u. value that must be taken from each pound of wet spent tan to

expel the moisture content. Therefore the net fuel value available would be:

$$3,325 = 790.76 = 2,534.24 \text{—say, in round numbers } 2,534 \text{ heat units.}$$

A good average grade of bituminous steam coal will have a thermal value of 13,000 B. t. u. per pound. Hence the relative value of the fuels would be as follows:

$$2,534 \div 13,000 = 19.5 \text{ per cent, or, say in round numbers, 20 per cent.}$$

Cost of coal being \$3.00 per ton, the relative value of spent hemlock bark would be $\$3.00 \times 20 \text{ per cent} = \0.60 per ton.

Obviously, this value will vary with the moisture content of the bark. The writer, however, believes it to be a fair average value for spent tan bark in the condition in which it is discharged from the leach.

One cord (2,240 lbs.) of air-dried hemlock bark, after leaching, will leave a wet residue having a gross weight of 4,856 lbs. Dividing this by 2,000, we have 2.428 tons, which, at 60 cents per ton, would be \$1.46, the value as fuel of the spent tan per cord of bark ground, when compared with coal of 13,000 B. t. u. value at \$3.00 per ton.

Production of Soda and Sodium Compounds.

In the production of soda and sodium compounds in the United States, figures reported by the United States Bureau of the Census show that the number of establishments was unchanged between 1909 and 1914. In each of those two census years the number was 68, although the output increased 41.7 per cent in quantity and 12.7 per cent in value. Reports for 1914 showed the production of 1,371,105 tons of sodas, valued at \$22,616,606. The output of these sodas in 1914 comprised 90,169 net tons of bicarbonate of soda, valued at \$1,439,014; 212,539 tons of caustic soda, valued at \$6,657,514; 106,591 tons of sal soda, valued at \$1,510,449, including 34,335 tons of sal soda crystals, valued at \$600,240; 935,305 tons of soda ash, valued at \$10,937,945; and 26,501 tons of borax, valued at \$2,071,774. At the census of 1909 there were soda products aggregating 967,730 tons, valued at \$20,061,505. The 1914 output thus exceeded that of 1909 by 403,375 tons in quantity, and by \$2,555,101 in value.

In addition to these sodas, there were manufactured in 1914 sodium products to the value of \$8,280,572, not including sodium chemicals, which latter—for example, chemicals used in the manufacture of photographic materials—are classified in connection with other industries. This production includes 169,049 tons of sodium silicate, valued at \$1,648,854; 11,824 tons of sodium bichromate, valued at \$1,125,398; 15,397 tons of sodium phosphate, valued at \$853,528; 20,263 tons of sodium sulphide, valued at \$516,644; 24,505 tons of Glauber's salt, valued at \$316,338; and concentrated lye, the product of compounders and packers, to the value of \$1,556,141.

PRICES OF CHEMICALS, OILS, ETC., JULY, 1916

WHOLESALE PRICES PREVAILING IN NEW YORK MARKET ON JULY 12

CHEMICALS, INORGANIC.

Acetate of lime, 100 lbs.	\$ 7.00 @ 7.05
Alum, ammonia, crystals, lb.	.05 @ .05
Aluminium sulphate, 100 lbs.	.04 @ .04½
Arsenic, white, lb.	.06½ @ .07½
Barium chloride, ton.	110.00 @ 115.00
Barium nitrate, kegs, lb.	.14 @ .16
Bleaching powder, drums, 100 lbs.	5.25 @ 5.50
Bleaching powder, drums, 100 lbs.	5.25 @ 5.50
Blue vitriol, car lots, 100 lbs.	10.00 @ .
Blue vitriol, powdered, 100 lbs.	18.00 @ .
Borax, car lots, f. o. b. N. Y., 100 lbs.	7.25 @ 7.50
Brimstone, crude, ton.	30.00 @ 35.00
Caustic soda, 74 to 76%, lb.	.04½ @ .05
Chalk, precipitated, casks, lb.	.03½ @ .05
Glauber's salt, bags, 100 lbs.	.65 @ .75
Nitric acid, 36 to 42°, 100 lbs.	6.25 @ 9.25
Phosphoric acid, 1.750 lb.	.30 @ .34½
Potassium bichromate, lb.	.40 @ .42
Potassium carbonate, calcined, 90 to 96%, lb.	1.00 @ 1.10
Potassium chlorate, crystals, lb.	.48 @ .50
Potassium cyanide, bulk, 100 lbs.	.45 @ .50
Quicksilver, flasks	83.00 @ 85.00
Silver nitrate, ounce.	.38% @ .40%
Soda ash, 48%, 100 lbs.	2.50 @ 3.00
Sodium acetate, lb.	.14 @ .15
Sodium bicarbonate, American, 100 lbs.	1.75 @ 2.75
Sodium bichromate, lb.	.31 @ .32
Sodium chlorate, 100 lbs.	.35 @ .40
Sodium hyposulphite, in bbls., 100 lbs.	2.00 @ 2.25
Sodium nitrite, lb.	.12 @ .14
Sodium sulphide, crystals, 100 lbs.	2.00 @ 3.00
Sulphuric acid, 60° and up, cwt.	1.50 @ 2.00
Sulphuric acid, 66°, ton.	35.00 @ 40.00
Talc, domestic, spot, ton.	15.00 @ .
Tin bichloride, 50°, 100 lbs.	13.75 @ .
Tin oxide, lb.	.46 @ .48
Zinc oxide, lb.	.15 @ .17

CHEMICALS, ORGANIC.

Acetanilid, lb.	.65 @ .75
Acetic acid, 28%, 100 lbs.	5.50 @ 6.00
Acetic acid, glacial, 99½% carboys, lb.	.45 @ .50
Acetone, drums, lb.	@ .
Alcohol, denatured, 188 proof, gal.	.57 @ .60
Alcohol, grain, 188 proof, gal.	2.70 @ 2.72
Alcohol, wood, 95%, gal.	.70 @ .72
Amyl acetate, gal.	5.50 @ 5.75
Benzoic acid, from tuluol, cwt.	7.00 @ 7.25
Carbolic acid, drums, crystals, lb.	.60 @ .75
Carbon tetrachloride, lb.	1.17½ @ .19
Chloroform, lb.	.50 @ .55
Citric acid, domestic, crystals, lb.	.67 @ .67½
Cresol, U. S. P., gal.	1.36 @ 1.50
Ether, U. S. P., 1900, lb.	.15 @ .20
Formaldehyde, 40%, carboys, lb.	1.11½ @ .12
Glycerine, dynamite, lb.	.45 @ .
Pyrogallie acid, crystal, lb.	2.65 @ 3.50
Salicylic acid, lb.	2.25 @ .
Tannic acid, technical, lb.	.60 @ .61
Tartaric acid, crystals, U. S. P., lb.	.66 @ .66½

DYE MATERIALS.

Acid orange, lb.	1.75 @ 2.20
Aniline oil, drums, imported, lb.	@ .
Aniline, domestic, lb.	.45 @ .55
Benzol (white), gal.	.80 @ .85
Bismarck brown, lb.	3.00 @ 5.00
Carmine, lb.	5.00 @ 5.25

Cochineal, silver, lb.	.77 @ .78
Cochineal, black, lb.	.81 @ .85
Gambier, lb.	.13½ @ .14
Indigo madras, lb.	.98 @ 1.00
Logwood extract, 51°, lb.	.35 @ .45
Madder, Dutch, lb.	.24 @ .25
Methyl, violet, lb.	8.00 @ 15.00
Methylene, technical, lb.	7.00 @ 10.00
Prussian blue, soluble, lb.	2.00 @ 2.20
Sulphur, black, lb.	.90 @ 1.90
Sulphur, brown, lb.	.40 @ .60
Zinc dust, prime to heavy, lb.	.28 @ .30
Zinc oxide, American, lb.	.14 @ .18
Zinc sulphate, lb.	.07½ @ .08½

ESSENTIAL OILS.

Almonds, bitter, lb.	12.50 @ 14.00
Amber, crude, lb.	14.00 @ 16.00
Anise, technical, lb.	1.00 @ .
Camphor, Japanese, 72 lb. cans, lb.	.17 @ .20
Cinnamon, lb.	18.00 @ 20.00
Clove, lb.	1.20 @ 1.25
Cubeb, lb.	3.25 @ .
Ginger, lb.	5.50 @ 6.50
Limes, distilled, lb.	2.75 @ 3.00
Pennyroyal, prime, American, lb.	1.65 @ 1.85
Peppermint, prime, American, lb.	1.80 @ 1.90
Spearmint, oz.	1.60 @ 1.75
Wintergreen, synthetic, oz.	2.25 @ 2.60
Wormwood, oz.	2.25 @ 2.60

FERTILIZER MATERIALS.

Ammonium sulphate, 100 lbs.	3.55 @ .
Blood, dried, N. Y., 100 lbs.	2.95 @ .
Blood, dried, f. o. b. Chicago, 100 lbs.	2.65 @ .
Bone black, sugar discard, ton.	.27 @ .30
Bone; oil discard, ton.	.18 @ .20
Muriate of potash, 80-85%, ton.	400.00 @ .
Phosphate, acid, per unit, ton.	80.00 @ 96.00
Sulphate of potash, 90%, ton.	275.00 @ .
Tankage, Chicago, 100 lbs.	2.50 @ .

OILS.

Castor oil, No. 3 bbls., lb.	.15 @ .
Corn oil, crude, 100 lbs.	8.41 @ 8.16
Corn oil, refined, 100 lbs.	10.41 @ 10.45
Cylinder oil, light filtered, gal.	.20 @ .25
Cylinder oil, dark filterel, gal.	.19 @ .20
Fusel oil, refined, gal.	6.00 @ 6.25
Linseed oil, carlots, gal.	.67 @ .
Menboden oil, crude, Southern, gal.	.48 @ .49
Naphtha, auto, 68°/72°, gal.	.33¾ @ .
Paraffine oil, high viscosity, gal.	.25½ @ .26½
Soya oil in bbls., lb.	.07¾ @ .08
Spindle oil, No. 1, gal.	.19 @ .20
Spindle oil, 20 gravity, gal.	.17 @ .18
Tar oil, commercial, gal.	.20 @ .22
Turpentine, gal.	.17½ @ .48

WAXES, ETC.

Beeswax, ordinary, pure, lb.	.30 @ .31
Ceresin wax, yellow, lb.	.10 @ .30
Ceresin wax, white, lb.	.14 @ .10
Japan wax, lb.	.15 @ .16
Paraffine, crude, 124-126 mp., lb.	.05¼ @ .05¾
Pitch, pine, first grade, bbl.	4.50 @ .
Rosin, P grade, N. Y., bbl.	5.70 @ 5.75
Stearic acid, extra quality, lb.	.15½ @ .17
Stearic acid, single pressed, lb.	.12½ @ .15
Stearic acid, double pressed, lb.	.13¾ @ .15
Tar, retort, bbl.	7.50 @ .

NOTES OF THE CHEMICAL AND ALLIED INDUSTRIES

Acid.—The United Zinc Smelting Corp. has obtained a 60-acre site at Moundsville, W. Va., and will utilize 24 acres for a 1,200x1,000 ft. plant. This will include a 350x250 ft. main structure, chemical factory, furnaces, gas producers, tile factory to supply furnaces, office buildings, etc. The structures will be of steel, brick and concrete construction. The first unit will consist of two blocks of furnaces and one unit of acid plant which will produce about 50 tons of 60 degree acid per day, and also some 60 degree acid, some battery acid and about 25 tons of spelter per day. F. J. Eckenfels, Moundsville, is chief engineer.

Acids.—The Trail Smelter, at Trail, B. C., in which the Canadian Pacific Ry. has a large interest, has started construction of a plant for the manufacture of sulphuric and hydrofluoric acid, which is expected to be ready for operation this month. A site is also being cleared for a copper refinery and the existing lead refinery will also probably be extended. The new plant for the manufacture of zinc is now in operation, though shipments have not yet commenced. The Cooper Converters now in course of installation are nearing completion and should be working shortly. The new lead mill is in operation and is working well.

Beet Sugar.—The Montana & Utah Sugar Refining Co. will construct a beet sugar factory at Hamilton, Mont. The company is now building a sugar factory at Grants Pass, Ore. About \$500,000 will be expended on the two installations.

Bleaching.—The Yadkin Bleaching Co., of Salisbury, N. C., has been organized mainly by cotton manufacturers and proposes the construction of a \$200,000 bleaching and mercerizing plant for textiles. The officers of the company are as follows: D. P. Campbell, New York, president; T. C. Love, Gastonia, N. C., first vice president; M. L. Jackson and N. B. McCauley, Salisbury, N. C., second vice president and secretary and treasurer, respectively.

Cement.—The Golconda Portland Cement Co., Golconda, Ill., has been incorporated with a capital stock of \$1,500,000 to manufacture cement, etc. The incorporators are H. G. Calkins, Edward B. Clark and Charles Durfee.

Cement.—The Cumberland Mountains Mineral Co. will erect a Portland cement plant at Cumberland Gap, Tenn., that will have a daily capacity of 30 carloads of cement and will represent an investment of about \$450,000. Victor Buetner, Holston Bank Bldg., Knoxville, Tenn., is president.

Chemical.—The French Society of Chemical Products, Detroit, Mich., has been incorporated with \$100,000 capital stock to manufacture chemical products. The incorporators are Claude Fraylein, George T. White and H. E. Marshall.

Chemicals.—The Michigan Electro-Chemical Co.,

Menominee, Mich., has been incorporated under the laws of Michigan by capitalists of Marinette, Wis., and Menominee to establish a plant and laboratory. The capital stock is \$150,000. Officers have been elected as follows: President, Edward Daniell, general manager, Menominee & Marinette Light & Traction Company; vice president, R. F. Goodman, Marinette; secretary, A. R. White, Marinette; treasurer, C. W. Gram, Menominee.

Chemicals.—Bristol Chemical Works of Bristol, Va., has been incorporated with a capital stock of \$50,000 and will manufacture chemical products used mainly by manufacturing druggists. J. P. Ray, Damascus, Va., is president.

Chemicals.—Seminole Chemical Co., of Jacksonville, Fla., has been incorporated with a capital stock of \$20,000. Fred W. Seewing is president and Henry Kleitman is secretary-treasurer.

Chemicals.—Mutual Chemical Co., of America, 55 John St., New York City, is reported contemplating building a large addition to its branch plant in Baltimore, Md.

Chemicals.—John T. Milliken & Co., St. Louis, Mo., has awarded a contract to the Kellermann Construction Co., of that city, for erection of a 4-story plant.

Chemicals.—The Bristol Chemical Works, of Bristol, Va., has been chartered with an authorized capital stock of \$50,000. The officers are J. P. Ray, Damascus, Va., president; A. P. Brinkley, Elk Park, N. C., vice president; and J. R. Patton, Elk Park, N. C., secretary and treasurer.

Chemical.—The Gasselli Chemical Co. has awarded the contract for the erection of a large research laboratory at Cleveland, O., to the Crowell, Lindoff, Little Co., of that city.

Coke Oven By-Products.—The Colorado Fuel & Iron Co., of which J. B. McKennan is general manager, has awarded a contract to a Pittsburgh concern for the erection of a coke oven by-products plant at Pueblo, Colo., adjoining the Minnequa steel plant. Preliminary work is now underway.

Cottonseed Products.—Alston Boyd of the Crescent Cotton Oil Co., Memphis, Tenn., and associates will construct a \$150,000 plant at Dallas, Tex., for the manufacture of cottonseed products. The mill will be equipped with six presses for a daily capacity of 100 tons of cotton oil. Machinery also will be installed for bleaching lint cotton for paper pulp manufacture. The preliminary arrangements are in charge of W. S. Fontaine, Dallas. E. B. Van Keuren, Birmingham, Ala., is the engineer.

Cottonseed Oil.—The Sulzberger & Sons Packing Co., Chattanooga, Tenn., will have work started shortly on the erection of a \$200,000 cotton oil mill at Chattanooga.

Cottonseed Oil.—A \$150,000 cottonseed oil plant

is to be constructed for Alston Boyd of the Crescent Cotton Oil Co., Memphis, Tenn., and others. Six presses with a daily capacity of 100 tons of cottonseed will be installed.

Drugs.—National Drug Co. has had plans prepared by Charles W. Denny, architect, Hale Bldg., Philadelphia, Pa., for a 3-story brick factory building to be erected at Wayne Junction, Pa.

Dyes.—It is reported that a dye factory will be constructed at New Orleans, La., by Robert Saunders, 7935 Burthe St., New Orleans.

Fertilizer.—International Agricultural Corp., 61 Broadway, New York City, has awarded a contract to Hugger Bros., Marine Band Bldg., Buffalo, N. Y., for rebuilding the fertilizer reduction plant at Buffalo, which was destroyed by fire.

Graphite.—Steps are being taken to organize a company capitalized at \$2,000,000 for the development of graphite in North Carolina. The plan provides for the construction of a manufacturing plant at Atlanta, Ga. New York, Canadian and Atlantic capitalists are interested. H. M. Ashe, Atlanta, is the secretary of the preliminary organization.

Ink Manufactures.—The Ault & Wiborg Co., ink manufacturers, Cincinnati, O., have plans underway for two additional buildings for its new chemical department now being established in the Ross Lake tract at 51 Bernard. The two structures will contain over 50,000 sq. ft. of floor space. The Ault & Wiborg Co. already has let contracts for four structures, and it is likely that the final plant will consist of 8 or 10 buildings.

Insulite.—The M. & O. Power Co. is planning to start construction at once on the erection of an insulate plant at International Falls, Minn.

Lead Hardening Plant.—Contracts will be let at once for the erection of a \$100,000 plant at Keokuk, Ia., for the hardening of lead by the process owned by the United Lead Co., a subsidiary of the National Lead Co. The plant will be erected adjacent to River Smelting & Refining Co. and will cost about \$100,000.

Molybdenum.—The International Molybdenum Co., Ltd., has begun work on the erection of a concentrator at Renfrew, Ore. It will have a capacity of 100 tons per day, and draw its supply of ore from mines at Mount St. Patrick, Enterprise, Wakefield and Sudbury. The concentrated product will be sent to a refinery at Orillia, but a refinery will be established at Renfrew as soon as the city can furnish the company with sufficient electrical energy. J. L. Murray and Herbert A. Jordan, both of Renfrew, are president and secretary-treasurer of the company.

Oxygen.—The Linde Air Products Co. began construction early this month on a \$100,000 plant at Birmingham, Ala.

Paper Mill.—Construction was started July 5 on a bleach mill to be erected at Elkton, Md., for the Jessup & Moore Paper Co. The new mill will be

built adjoining the company's pulp works along the river front and will cost approximately \$400,000.

Phosphate.—Electric Reduction Co. has awarded contract to Foundation Co., Montreal, Que., for erection of a \$50,000 phosphate manufacturing plant at Buckingham, Que.

Pine Oils, Tars, Etc.—The Schauman Chemical Co., of Beaumont, Tex., organized recently with H. D. Fletcher as president, will build \$5,000 plant to manufacture pine oils, tars, turpentine, wood preservers, etc.

Potash.—The Potassium Manufacturing Corp. has taken steps for the erection of a potash reduction plant at El Segundos, Cal. The first unit will cost about \$40,000 and will include laboratories, three drying rooms, machine shop, warehouse and storage building.

Pyrotone.—The Pyrotone Chemical Co., of Dallas, Tex., has been incorporated with a capital stock of \$20,000, the incorporators being C. I. Fulson, J. M. Brooks and L. H. Flewelen.

Pulp.—Hawley Pulp & Paper Co., of Oregon City, Ore., is having plans prepared for a second unit to its plant.

Pulp and Paper.—Great Southern Lumber Co., of Bogalusa, La., will expend \$200,000 for buildings and \$600,000 for equipment for a pulp and paper mill. It will have a capacity of 60 tons of pulp and 100 tons container lines. W. H. Sullivan is general manager.

Pulp.—The Tropical Lumber & Pulp Co., chartered last month with a capitalization of \$500,000 and headquarters at Baltimore, Md., proposes the development of 125,000 acres of timber in Dutch Guiana. It is possible the company will build paper pulp mill in future. John J. Duffy, 2100 Lafayette Ave., Baltimore, Md., general manager of the Lafayette Mill & Lumber Co., is president of the new company.

Pulp.—A plan is under consideration for the construction of a pulp and paper mill at Marshfield, Ore. The scheme also proposes installation of hydroelectric plant, by-product plant and creosoting works. W. J. Wiley, Portland, Ore., is interested.

Quartz Mill.—The H. M. Byllesby Co., Chicago, Ill., owners of the Ragged Top tungsten claims, will erect a \$100,000 mill at Toulon on the Southern Pacific Ry., and will take on custom ores. The headquarters will be at Lovelock, Nev. During the 60 days the Byllesby Co. has been working on the ground it is stated to have taken out and shipped 550 tons of ore.

Rosin and Turpentine.—The Rosin & Turpentine Export Co., of Georgia, has been reorganized with an authorized capital of \$2,500,000. The existing company has surrendered its charter granted in Delaware and has obtained a Georgia charter. The American International Corporation of New York has become a subscriber to a controlling interest in

the organized company and George J. Baldwin, of New York, president of the International, will be a vice president of the export company. Other vice presidents are W. F. Coachman, of Jacksonville, Fla., and Charles W. Bowring, of New York. J. A. G. Carson, of Savannah, president of the Carson Naval Stores Company, is president of the reorganized company.

Rubber.—The Miller Rubber Co., of Akron, O., has announced plans for an 8-story factory building as an addition to its present plant.

Silk.—Susquehanna Silk Co. has awarded a contract to Reinard Bros., Bloomsburg, Pa., for erection of a 5-story 250x175 ft. steel and brick addition to its plant at Sunbury, Pa.

Silk.—The Viscose Co., Marcus Hook, Pa., is to construct a mill at Roanoke, Va., to have an initial weekly capacity of 40,000 lbs. of artificial silk. The contract for the buildings was awarded a few days ago to Irwin & Leighton, Philadelphia, Pa. Balinger & Perrot, Philadelphia, Pa., are the architects and engineers. The plant will comprise the following structures: 5-story 153x77 ft. building, with columns, floors and roof of reinforced concrete (flat slab construction), rolled steel windows and freight elevator; 1-story 536x140 ft. building (brick walls and shed construction), with roof of saw-tooth skylights, and cast-iron columns and steel trusses, with plank roof covered by composition roofing; 3-story 166x58 ft. building of reinforced concrete, flat slab construction similar to 5-story structure; 2-story and basement 154x143 ft. and 103x73 ft. structures with brick walls and generally of reinforced concrete construction, with composition roofing; 108x70 ft. power house with brick walls and overhead coal bunkers; 191 ft. radial brick chimney, 11½ ft. inside diameter; 1,077,000 gal. concrete reservoir.

Sulphur.—Bids have been opened for the construction of the first \$50,000 unit of a sulphur refinery for the Freeport Chemical Works of Freeport, Tex. This company is controlled by the San Francisco Chemical Co., of San Francisco, Cal. The installation will include furnaces and electric motors for an initial daily production of 50 tons of refined sulphur, flowers of sulphur and rock sulphur. The raw product will be obtained from the Freeport Sulphur Co., which is now installing additional units to its plant to increase the annual production to 600,000 tons.

Sulphur.—The West Texas Sulphur Co., organized recently, will develop 600 acres of sulphur property at Pecos, Tex. The present plans call for a first unit of an annual capacity of 100,000 tons. The officers of the company are as follows: F. M. Dancy, president; W. H. Hines, secretary-treasurer; Chas. E. Doddridge, general manager, all of 1034 Widener Bldg., Philadelphia, Pa., and W. H. Beard, Mobile, Ala., vice president.

Sugar.—United Fruit Co., Board of Trade Bldg., Boston, Mass., has approved plans for a \$1,500,000 sugar refining plant to be erected at Charlestown, Mass. It will consist of six steel and concrete buildings.

Tannery.—Bulls Ferry Chemical Co. has awarded contract for alterations to its tanning building at Shady Side, N. J.

Waterproofing Products.—The American Chemical & Manufacturing Co., of Norfolk, Va., has increased its capital from \$50,000 to \$200,000.

White Lead Substitute.—The Mineral Refining & Chemical Co. has awarded a contract to the Fruin-Colnon Contracting Co., St. Louis, Mo., for the construction of a plant at St. Louis, Mo., to consist of eight wood and one stone buildings. The plant will have a daily capacity of 50 tons of a substitute for white lead. This company has been incorporated with a capital stock of \$2,000,000. Havana and New York capitalists are interested. Joseph Mariman, Havana, is president, and M. J. Mandulay of Havana is a director. R. Bonastre, New York City, also is interested.

Wood Fiber.—Preliminary steps are being taken for the erection of a \$750,000 wood fiber plant at Hattiesburg. The city has donated a 42-acre site for the project. C. H. Wood, president of River Raisin Paper Co., and George R. Wright, vice president of the Louisiana Fiber Board Co., of Bogalusa, La., are interested.

Zinc.—A plan is under consideration to establish a smelting plant for the electrolytic reduction of zinc ore in Spokane, Wash., at a cost of \$500,000. Jap P. Graves, J. P. McGoldrick, George Turner, J. D. Sherwood and Walter J. Nicholls, all capitalists of Spokane, are back of the enterprise. J. O. Pateneau, inventor of a refining process, is also a promoter.

Zinc.—The Mammoth Copper Co., Kennett, Colo., will erect a plant for recovering zinc and other metals by an electrolytic process.

Zinc.—The United Zinc Smelting Corp., New York, has purchased 60 acres of land at Moundsville, W. Va., and will have construction started shortly on the first unit of a \$1,000,000 plant. It will be 1,100 by 1,200 ft. in dimensions, constructed of steel, brick and concrete, and will be, it is said, the largest one of the company. The United Zinc Smelting Corp., of which M. M. Pearlman is general manager, owns mines at Joplin, Mo., and smelters in Illinois and at Clarksburg, W. Va.

According to the annual statement of the Geological Survey on abrasive materials in 1915, now available for distribution, the value of natural abrasives produced and marketed in the United States during the year reached \$1,662,055.

Chemical Engineer and Manufacturer

Vol. XXIV.

AUGUST, 1916.

No. 2.

PUBLISHED MONTHLY by the MYRON C. CLARK
PUBLISHING CO..

608 S. Dearborn Street, Chicago

*Entered as Second Class Matter, Aug. 19, 1907, at the Post Office
at Chicago, Illinois, under Act of March 3, 1879.*

Subscription—United States, Cuba and Mexico \$2.00
Extra postage to Canada 25c a year; to foreign countries 50c a year.
Remittances may be made by check, draft or money order in favor of
CHEMICAL ENGINEER AND MANUFACTURER

All communications should be sent to CHEMICAL ENGINEER AND
MANUFACTURER, 608 S. Dearborn Street, Chicago, Ill.

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EFFECTIVE PUBLICITY AS AN AID TO CHEMICAL PROGRESS.

Without the support of capital great progress in industrial chemistry is not to be had. But capital, for the most part, must be secured from an investing public in the form of stock subscriptions and bond purchases. To be induced to invest the public must at least possess some degree of familiarity with the nature of the plant and its product, in addition to confidence in its managers. Publicity is an essential means of teaching the public what chemical engineers have accomplished and what they may be expected to accomplish. Therefore, no opportunity should be missed by chemical engineers to reach the public through the columns of the daily press and popular magazines.

In this issue we reprint a letter by Arthur D. Little, ex-president of the American Chemical Society. The letter was published in the *Philadelphia Ledger*, and is a splendid sample of effective publicity. Even to some chemical engineers this letter will be news in some of its parts. Certainly to most business and professional men it will come as a surprise to learn to what extent chemical research has already developed in America.

There is scarcely a daily paper that will not gladly print a letter so interesting and instructive as this letter of Mr. Little. We suggest that every chemical engineer try his hand at writing a letter now and then to the editor of his home town paper. Stories that are relatively old to chemists will usually be entirely new to the public. For example, the story of the invention of the "gas-filled lamp" by the research staff of the General Electric Co. is probably unknown by 99 per cent of all editors of daily papers, and it is an excellent story involving both chemistry and physics.

The automobile has given to many people a keen interest in the steel alloys. Not one of the new alloys is without a "story" as to its discovery and commercial development. Tell the "story" in popular language and it will find thousands of readers.

Engineers of all classes are coming out of their shells—their technical accretions—and by appearing before the public both as men and as economists are forcing a belated public recognition of the true worth of engineering. Chemical engineers should not be outdone by their professional brethren in the other branches of engineering practice.

DAILY PAPER EDITORIALS ON SIR WILLIAM RAMSAY.

Few of the metropolitan daily papers have failed to comment editorially on the death of Sir William Ramsay. Of the editorials that have come to our desk none shows a better conception of Ramsay's achievements than the one reprinted below, from the *Philadelphia Ledger*. We are inclined to think that the editorial was written by a chemist. The simile in its opening sentence would alone indicate as much.

In this connection we may well call attention to the fact that several of the largest daily papers have engineering editors, men competent to write appreciatively and intelligently on technical matters. Doubtless the practice of employing such editors will grow. Many an engineer could probably secure part time employment as a technical editor on a daily paper. Even if the compensation were nominal the experience would be valuable, but more important than the experience is the worthwhile publicity thus to be secured for the whole engineering profession. Every such editorial as the one here quoted is a step toward popular appreciation not only of the pure scientist but of the engineer who applies the discoveries of such men as Sir William Ramsay:

Ramsay and the New Chemistry.

The death of Sir William Ramsay gives a date to the new chemistry, since about his name and fame as crystals around a rod in the mother liquor there attach the astounding discoveries of intra-atomic activities and the interchangeability of matter that make modern chemistry, with all its precision and its exact processes under fixed laws, at times read like the vagaries of the Middle Ages, when men believed in the "philosopher's stone" as the universal solvent. For it was by reason of the stir made in the world of science everywhere by the discoveries of the properties of the Roentgen rays, as well as the isolation of the rare gas argon from nitrogen in 1895 by Ramsay and Lord Rayleigh, that the physicists and chemists and electrical specialists began that new weighing of all things and that race for the examination of what went on in the very inside of the atoms themselves, instead of molecules, that led to the discovery of radium in 1898 and the opening up of a new world of research through radioactive substances.

No watcher of the skies, nor Cortez "silent upon a peak in Darien," felt a greater thrill than did the savants who, carrying on the sane traditions of Sir Humphry Davy and Faraday as to the exact study of natural and chemical phenomena, through their most delicate observations, including a precision of weighing that forecast the presence of an unknown element, were finally rewarded by the thing itself. And if the discovery of argon meant little in the larger chemical field, when helium and its associated gases were found later, and then, after radium had upset all preconceived theories as to the behavior of matter and of energy, when there came the demonstration that radium in disintegration produced helium, the transmutation of the elements, the alkahest of the older philosophers, seemed indeed within reach. And this work of Ramsay's—what with the electrical theory of matter with its ions and its electrons within the atoms, which, under the scrutiny of the new chemistry, seemed to take on the character of immense spheres instead of immeasurably small particles—made up the new chemistry.

Twenty years has seen the rise of new and newer problems, and the scientists of today, who owe so much to the patience of Ramsay and his penetrating generalizations, are but on the threshold of the discoveries that will prove the inter-relationship of all the elements even if lead cannot become gold in the crucible under our eyes. Ramsay was a true disciple of the British chemists, who sowed where the Germans have reaped commercially, and he deserved all the honors that came from the worldwide recognition of his primacy as an observer whose seeing eye was reinforced by the analyzing brain with few superiors.

ENGINEERING DEFINED.

Attempts to define engineering have been numerous. No definition has had wider circulation than the one formulated by Tredgold and adopted by the Institution of Civil Engineers in its infancy: "Engineering is the art of directing the great sources of power in nature for the use and convenience of man."

Gillette, in his "Handbook of Cost Data," calls attention to the absence of the word economics in Tredgold's definition, and he also points out that even an uneducated farmer would be classed as an engineer if Tredgold's language were taken literally. Gillette says:

"I object to this definition not so much upon the ground that it includes too much as upon the ground that it fails to include what it should, namely, the fundamental function of the modern engineer, which is to solve problems in economic production."

He then proceeds to give a modern definition thus: "Engineering is the conscious application of science to the problems of economic production. Under this definition, which may ultimately be regarded as too broad, I am to include that part of engineering which relates to the scientific management of men, and the scientific development of methods of construction and operation, as well as the design of the most economic structures and machines for a given service."

There are few, we think, who will find much to criticize in this modern definition of engineering. But there are still many teachers of engineering who have yet to appreciate fully the commercial element that all good engineering exemplifies. As indicative of this, note how rarely a course leading to an engineering degree contains even the most elemental part of an economist's training, namely, accounting and cost keeping.

Our engineering colleges have not yet entirely outgrown Tredgold's definition of engineering wherein the word economics is conspicuous by its absence.

During 1915 secondary metals were recovered from scrap, sweepings, etc., in the United States to the value of \$114,304,930, according to the annual statement on Secondary Metals issued by the U. S. Geological Survey. This report is now available for distribution.

SOURCES OF NITROGEN COMPOUNDS IN THE UNITED STATES.

An interesting publication on the sources of nitrogen compounds in the United States has been issued recently by the Smithsonian Institution. The pamphlet was prepared by Chester G. Gilbert and it points out in a general way the nature of the problem confronting this country. Mr. Gilbert's paper, practically in full, follows:

With the extension of chemical needs such as are offered by the development of cyaniding in metallurgy, and of refrigeration in the preservation of foodstuffs, and more especially with the extension of the need for artificially provided fertilizers, nitrogen compounds have come to be necessary not only to the welfare, but to the very existence, of a people living under modern conditions of economic development. At the outset the Chilean mineral nitrate deposits bore the brunt of the responsibility in providing for these growing needs; but more recently the gradual development of the by-product feature in chemical industries, more especially in the field of coal products, has introduced a very material competitor with the natural sources¹, matching their two and a half million tons of annual output in nitrate of soda with around two million tons of sulphate of ammonia. Even the combined sources have, however, proven insufficient to maintain reserves with which to meet the world's ever-increasing demands. In 1898 Sir William Crooks called attention to this inadequacy and pointed to atmospheric nitrogen fixation as the only preventive remedy for an impending economic breakdown. Recent events have emphasized the truth of this prediction, and brought the United States to a consideration of its national responsibilities in this direction.

Various means have been evolved in the chemical laboratory for effecting the fixation of atmospheric nitrogen through enforced combination, such as that with atmospheric oxygen or with hydrogen, both of which resultant combinations are absorbable in water to form nitric acid and ammonia water, respectively. Nitrogen, however, owing to the extreme inertness of its gas molecule, is difficult to stimulate into combination, and as a result most of the processes evolved have been found to offer such little encouragement toward efficient commercial practicability that to include all of them in any purely industrial discussion would serve only to introduce so many profitless elements of complexity. Accordingly, while any one of the several other processes of more or less claim to merit may in some future time force its way to the front over what seem now to be insurmountable obstacles, there are today only three methods which have stood up under commercial test sufficiently to warrant definite consideration in a summary discussion. The three are known as the arc method, the cyanamide process, and the Haber process of nitrogen fixation. Adding then the coal products source of fixed nitro-

gen, there are four currently prominent commercial sources of fixed nitrogen available for development to meet varying needs within the country.

1. ARC METHOD.

If a current of air be passed through an electric arc some of the oxygen and nitrogen of which the atmosphere is composed enter into chemical combination as oxides of nitrogen, which may then be treated chemically for complete oxidation and absorbed in water to form nitric acid. Thus a limitless source of the requisite ingredients is provided right on the spot without the least cost whatever; the chemistry involved is apparently of the very simplest, most direct order, and, moreover, the method is in actual operation on a commercial scale. Superficially, therefore, the project would seem to be just about ideal, and presents one of the most alluring prospects offered in the field of chemical technology. The underlying difficulties in this problem are to be found in the inherent fact that nitrogen is chemically inert and extremely difficult to stimulate into the activity of entering into combination. This fact is forced home by the reflection that throughout the ages of the earth's existence its atmosphere has consisted of the self-same oxygen and nitrogen most intimately mixed, and had there been the least susceptibility on the part of the nitrogen, its complete combination with the oxygen would long ages ago have been effected, and instead of our now being engaged in trying to make them combine, there would be an atmosphere devoid of life-sustaining oxygen, and in place of water our oceans would be of concentrated acid. That same property of chemical inertness on the part of nitrogen which is the salvation of life itself on the earth has proven well-nigh disastrous to the commercial practicability of the arc method of nitrogen fixation, owing to the enormous electric power consumption involved.

In its present state of efficiency the arc method operations require roughly 2.75 to 3.00 H. P. year of electric power per ton of nitric acid yield.¹ Now the average private cost of power-site development in this country has been over \$120 per horsepower. Counting an operative interest rate of 8 per cent to finance the development proposition, and then including the other necessary items of depreciation, overhead charge, etc., a total of 12 per cent or 13 per cent on each horsepower of development, or about \$15 per horsepower year, is a fair estimate of costs under present-day conditions in this country. Then the 2.75 H. P. requisite for the fixation of the nitrogen in one ton of nitric acid means a cost, roughly, of over \$40 per ton of product in power expense alone.

¹The atmospheric nitrogen fixation industry is still in its first stages of evolution, and the figures available for the various processes are only such as are divulged from sources still actually involved. Moreover, the whole proposition is one offering no criteria for estimates other than those derived from actual operations. Accordingly, no credit for originality belongs with the publication of this paper, and, on the other hand, the only responsibility is for an honest attempt at interpretation. Every care has been exercised in checking up figures before their employment, and there is every reason, short of actual operative proof, for their acceptance.

The item of \$40 per ton of nitric acid, it must be remembered, takes into consideration power costs alone, and, moreover, represents a product for which under ordinary conditions there is no great market, so it would have to be converted to calcium nitrate for use as fertilizer. But calcium nitrate absorbs moisture with avidity, and has not proven itself adaptable to American fertilizer requirements where the cost of labor renders mechanical sowing desirable; and, moreover, its fertilizer equivalent in Chile nitrate of soda is already available at around \$40 per ton, so the arc method cannot be made to stand on its own feet in this country under present conditions to the extent of contributing significantly toward the country's material well-being. Owing to the opportunity for securing lower interest rates, it would be possible for the Government to develop power at a much lower cost, commonly estimated at \$8 per horsepower year. This would cut the power costs to around \$22 per ton of nitric acid, but even then the enormous power requisites and the inadaptability of the product remain as unsurmounted obstacles.

The Government has under consideration at this writing a \$20,000,000 project for atmospheric nitrogen fixation primarily as a military measure, and it may be of interest in passing to interpret the efficiency of such a project in terms of the hydroelectric arc method. If the entire sum were to be put into power-site development, it would furnish somewhere around 150,000 H. P., capable of yielding in the neighborhood of 50,000 tons of nitric acid, or about one-fourth the estimated military emergency requirements alone; and at that, the entire cost of the plant installation and operation, running into the millions of dollars, would have to be additional. To satisfy Government estimates of around 200,000 ton war-time requirements would entail a power generation of around 600,000 H. P., or some 50,000 H. P. more than the total Niagara power development. Such a project would cost around \$80,000,000 to eventuate, and in its operation during peace times as an agricultural proposition in competition with other sources would necessitate an annual subsidy running into the millions of dollars, without offering a single advantage excepting as a preparedness measure. Norway, with three or four dollar power, has been able to develop the arc method on a self-supporting basis, but with a power consumption of around 3 H. P. per ton the difference between \$3 and \$15, or even the possible \$8 of Government cost, is precisely that between success and failure.²

II. CYANAMIDE PROCESS.

The so-called Cyanamide process of nitrogen fixation is dependent upon the fact that calcium carbide may be induced with comparative ease to absorb nitrogen, thus forming a combination of calcium, carbon

and nitrogen, known commercially as cyanamide. Thus, unlike the direct arc product, cyanamide involves raw materials in the form of limestone and coal, or, rather, their derivatives, lime and coke. The lime and coke are fused together to form carbide, which is then inserted in finely ground condition in an electric furnace where a temperature of 1,000° C. is maintained, while a stream of nitrogen gas already separated out from the oxygen of the air is fed in and absorbed by the powdered carbide. The product is a mixture of cyanamide, excess carbide, and lime, which, after being hydrated to get rid of the free carbide and caustic lime, is ready for the market as nitrogen-bearing fertilizer. By treating this cyanamide with superheated steam its nitrogen may be released to enter into combination with the hydrogen of the steam, forming ammonia, which, if desirable, may in turn be burned with air to form nitric acid.

Thus the Cyanamide process affords three main products in direct sequence from the raw ingredients employed, namely, cyanamide, ammonia, and nitric acid, with nitric acid the end point instead of the first product to be derived, as is the case with the employment of the arc method. Carrying the process clear through to the nitric acid stage, the power consumption is approximately $\frac{1}{2}$ H. P. year per ton of nitric acid, or about one-sixth to one-fifth that requisite for the arc method; the raw materials employed are roughly a half ton each of lime and coke; the labor items involved in the two processes are to all practical purposes equal; and the normal peace time first product from the Cyanamide process, calcium cyanamide, has proven thoroughly applicable to agricultural use. Comparison of the two processes with reference to their relative values toward meeting the country's needs offer, first of all, a saving of four-fifths to five-sixths the power consumption in favor of the Cyanamide process. To appreciate the significance of this item it is only necessary to reflect that, whereas the country's estimated 200,000 tons requirement calls for a power supply of over a half million horsepower year in the one case as against one of only 100,000 H. P. year in the other, the difference is not merely one of economics, but of availabilities as well. Again, the normal product from the arc method is one whose chief demand is founded upon abnormal war times, while the normal first product from the other is an agricultural one, fitting into normal conditions. Again, the regular product from the arc method is not convertible to meet peace-time requirements adequately, while the product from the other is readily convertible to the emergency nitric acid form. Standing alone in prominent opposition is the fact that raw ingredients enter into the manufacture of the cyanamide product; but even this one opposing element will hardly loom so conspicuously when the carbon electrode consumption involved indirectly in arc method procedure is considered. Ignoring indirect elements, however, the raw materials employed entering into

²It is to be borne in mind throughout this paper that any and all estimates and deductions refer purely to developments of nationally significant scale, and have not the least bearing upon the feasibility of localized private enterprises with the special opportunities which may be afforded. The one attempt to apply an arc process in this country, the purely experimental one at Nitrolee, South Carolina, may, however, be quoted in substantiation.

cyanamides involve a resource expenditure about the equivalent of a fifth that of arc method power under average American conditions. The difference between the two in significance amounts to that of three-fifths to two-thirds of the total power involved in arc method manufacture, plus the value of a product normally in demand as against that of one for which there is very little normal demand.³

HABER PROCESS.

Bearing in mind that ammonia is a chemical combination of nitrogen and hydrogen in the ratio of one atom of the former to three of the latter, synthetic ammonia would result if a properly proportioned mixture of the two gases in purified condition can be prevailed upon to react chemically. With the two essential ingredients readily available, the one from air, the other from water, the only problem is that of inducing chemical reaction. By what is known as the Haber process a means of effecting the necessary stimulus has been provided, and the Haber process of fixation is on a commercial basis in Germany, where, from the last available figures, it was netting at the rate of about 200,000 tons of ammonium sulphate per year. The agency for combination employed in the Haber process is compression of the mixed gases in the presence of a catalyzing agent. This results in a partial combination of the two gases to form ammonia, which may be absorbed out and the uncombined portion of the original gaseous charge returned for renewed treatment. The process does not make the high demands on electrical power required by the other processes of atmospheric nitrogen fixation in use, but involves technical difficulties in the way of manipulation which have prevented the proportionate extension of its use, even in Germany under present exigencies. No opportunity for an analysis of comparative costs is available, but the fact that the use of the process has not been extended proportionately even in Germany, where cheap skilled labor and military exigency have combined to give it every advantage over conditions in this country, may well be taken as evidence that the process has not yet been perfected to a point where it is able to qualify for final consideration.

BY-PRODUCT AMMONIA.

Mention has already been made of combined nitrogen as a by-product from chemical industries based upon the products of organic life both of the present day and of the geologic past; and coal-product operations were cited as the most advanced forerunner in this direction. With the wastefulness of method characteristic of American industrial practice, by-product development, even with reference to coal, has been unreasonably slow, and out of a possible 700,000 tons

the actual combined nitrogen recovery in the form of ammonium sulphate is only about 225,000 tons. Of late, however, the rate of increase has been stimulated to such an extent that with the completion of the by-product ovens now building the annual capacity for output will be around 400,000 tons, and it is fair to assume that if the tendency is unchecked by external influences the full coking yield of ammonia will be available to the country's use within the next few years.

The actual development of combined nitrogen returns from other by-product directions has been negligible, and they assume significance only in their possible bearing upon the future establishment and growth of industries important to the country's welfare. From this viewpoint their potential significance is scarcely less real than it is with reference to by-product coking. This country is bound to be the greatest coke manufacturing one in the world, and the desirability of developing the enormous by-product possibilities thus opened up, entirely apart even from the half million to million tons of ammonium sulphate now directly under consideration, is scarcely to be overestimated. The country cannot afford to take any step which will further hinder progress along these general lines.

The normal first product from the arc method of atmospheric nitrogen fixation is nitric acid; that from the Cyanamide process is calcium cyanamide; that from the Haber process is sulphate of ammonia; and that of by-product derivation is also ammonia, either in the form of ammonia liquor or ammonium sulphate. For munitions use the acid form is required, while agricultural and other more usual requirements employ either ammonium sulphate or some other neutralized form of combined nitrogen. The original character of first product is not necessarily of any great moment, however, in view of the fact that, once fixed, the form of combination is susceptible of change. Thus, the original nitric acid of the arc method may be neutralized to a nitrate salt, usually that of calcium because of the cheapness of the calcium source in limestone; cyanamide may be forced to yield up its nitrogen in the form of ammonia, which in turn may be oxidized to nitric acid; and the same is true of the Haber process sulphate. By-product ammonia, however, offers at present an obstacle to such flexibility of application, in the form of impurities which stand in the way of effecting the delicately balanced reactions involved in the oxidation of ammonia to nitric acid.

In view of the feasibility of effecting chemical readjustments, the problem before the country is not one purely or even primarily of military exigency, but rather of agricultural betterment with military reservations. The country is capable of absorbing an indefinitely greater amount of nitrogen compounds agriculturally, and of doing so to ever-increasing advantage to all concerned, provided only there is no sudden glutting of the market demand for it and that the cost is maintained sufficiently low to put a premium on intensive land cultivation. The real problem,

³Since power cost is the dominant item of expense in the arc method, while it represents only about a third of the fundamental expense connected with the cyanamide method, it is obvious that as power costs are reduced the purely financial aspects of the two methods converge. These converging lines cross at the point indicated by \$5 power. It would seem, however, out of the question that under present-day conditions power on sufficiently huge scale to carry a significant arc process plant is capable of development in this country, and, accordingly, the fact of convergence toward a \$5 H. P. per year point, while interesting, can hardly enter as a determining factor.

then, is that of developing sources of combined nitrogen such that their costs will not, as they do today, counterbalance the farmer's returns, making intensive effort profitless, and at the same time of avoiding any such precipitancy of action with reference to new sources as will tend to demoralize the market. If it fails to do the former, now that the matter has come up definitely for action, it will be failing to meet national responsibility of the greatest importance; if it fails to do the latter, consequences as disastrous to the country's welfare as any nitrogen shortage will result in the further hindrance of by-product development.

The nitrogen situation is one involving the whole structure of the country's economic development. Off hand, exception may be taken to this assertion on the grounds that the fundamental issue is one of military importance and may well be kept within those confines. Let any one who is disposed toward such an opinion evolve a solution whose efficacy is based purely upon a military need; then let him proceed to work out a balance sheet covering the operation of the resultant project over a period even of only five years. The scope of the issue broadens to include an agricultural aspect. Since nitrogen compounds may be prepared which are convertible between agricultural and military needs, and since an adequate nitrogenous fertilizer supply constitutes an invaluable economic asset, it may appear next that the situation resolves itself fixedly into the mere problem of determining the means calculated to provide the largest output of convertible nitrogenous compounds at the least cost. But industries no less important than a nitrogen-fixation one to the country's economic balance are involved in this field, and any governmental action in the nitrogen situation which would be disastrous in its effect on private initiative in the related industries would be inadvisable. Thus the scope of the issue widens not only beyond the strict confines of military need, but beyond those of agriculture as well, and action, to be of well-founded, permanently constructive value, must take cognizance of the whole situation.

SUMMARY.

To summarize a situation of such magnitude adequately in a few pages is not only difficult, but becomes increasingly so the more it unfolds with study. Accordingly, in the foregoing pages the aim has been rather to point out in a general way the nature of the problem confronting the country than to attempt any analysis of its various factors, much less to offer any complete solution. In substance, the following expressions with reference to conditions and the inferences seemingly afforded are offered:

Nitrogenous compounds are essential not only to self-defense but to the country's capacity for self-support, and to be effective the source must be such that the product may be adaptable to meet either requirement.

The arc method has not thus far demonstrated

capacity to meet the agricultural requirement at all, or even the defense requirement efficiently.

Definite knowledge concerning the Haber process is lacking, but its record of achievement is against it, and it would seem, moreover, unsuited to American conditions, at least in the present state of its development.

The Cyanamide process is capable of a development which will meet the requirements for a cheapened nitrogenous fertilizer source whose form of nitrogen content is readily convertible to nitric acid. The process is already a prominent factor in the economic well-being of most countries of older civilization, and is capable of similar extension in the United States.

By-product coking operations afford a source of nitrogenous compounds netting the country an annual production at the rate of over 200,000 tons of ammonium sulphate now, and due to raise this total to about 400,000 tons with the completion of the ovens now building. A total of about 700,000 tons would be possible if all coking were of by-product nature, and this total should be attained within the next few years. No practicable means for its oxidation to nitric acid have yet been found in this country.

By-product ammonia constitutes the country's one actual asset in the form of nitrogenous compounds. It has a rapidly growing yield of very great importance in itself, but of even greater importance as a factor contributing largely to the commercial possibilities of a number of industrial lines, especially that of coal products. The country cannot afford to run any risk of checking development along these lines.

The evolution of a practicable process for the oxidation of by-product ammonia to render present resources available, with the development of an atmospheric nitrogen fixation output by the Cyanamide process carefully timed to meet growing demands following a reduction in the retail price of nitrogenous fertilizer, would appear to be the desirable governmental procedure as being the one least liable to disastrous consequences.

Starting a Beet Sugar Industry in Siberia.

The beet sugar section of the Society of Siberian Engineers has started to organize trial sowings of sugar beet in Siberia to ascertain whether it is possible to develop a sugar industry in that country. It is planned to make the experiments cover three years. For this purpose the best grades of beet seeds have been obtained from European Russia and instructions have been drawn up with regard to the sowing of the seed, the care of beet plantations, the preparing of the soil for this purpose, etc. A specialist will be engaged to look after the trial plantations of sugar beet, which will be under the direct control of this expert beet grower and his assistants. The trial plantations will cover sections of 240 square sazhen (0.27 acre) each. The entire organization of such beet plantations will be under the supervision of S. W. Lebedeff, professor at the Tomsk Technological Institute.

LABORATORY STUDIES ON SECONDARY SULPHIDE ORE ENRICHMENT.

Investigations on the synthesis of the copper sulphide minerals and their decompositions and mutual transformations have been made by S. W. Young and Neil Preston Moore. The results of the first of these investigations are given in a paper in the June issue of *Economic Geology*, from which the following matter has been abstracted:

The researches have resulted in the synthesis by very simple methods of covellite, chalcocite and chalcopyrite, and possibly, although not quite certainly, of bornite. The great majority of the mineral syntheses in this field have heretofore involved the use of high temperatures, either fusion or heating in the autoclave from 150 to 400° C. The geological evidence seems to show conclusively, however, that most secondary enrichment has taken place below 100° largely probably between 20 and 50, and sometimes as low as zero in frozen water-saturated beds. It was deemed advisable therefore to carry out the experiments at temperatures more in conformity with natural conditions. The investigators, however, permitted themselves to improve on nature (probably) in the matter of the concentrations of some of the mineralizing reagents used. As most of the reactions with which they are concerned are very slow, this use of very high concentrations of certain "mineralizers" is necessary in order to obtain results within a reasonable time.

The paper contains the results of a rather extended investigation of the conduct of natural chalcocite, covellite, chalcopyrite, and bornite in alkaline, neutral and acid solutions, in the presence of a maximum concentration of hydrogen sulphide at 30° C. The maximum concentration of hydrogen sulphide was maintained by liquefying and sealing up some of the gas in a tube with the mineral and other reagent. The temperature was maintained by means of a thermostat, and 30° was necessary since at lower temperatures the crystalline hydrate ($H_2S \cdot 6H_2O$) appears as an ice-like mass, solidifying the whole contents of the tube, and making observations impossible.

EXPERIMENTAL METHODS.

The general method of procedure in these experiments was as follows:

A large number of glass tubes, fairly thickwalled, of an inside diameter of about eight millimeters, and a length of about twelve centimeters were sealed off at one end. Fragments of the minerals to be investigated were placed in the tubes, which were constricted near the open end to facilitate sealing off later. A sufficient amount of the aqueous solution of the reagent to be employed was introduced through the constriction by means of a thin capillary tube, and the tubes and contents were placed in an ether bath which was cooled to below the liquefying temperature of hydrogen sulphide by means of liquid air. While thus cooled, a stream of hydrogen sulphide from a generator was passed into the tube. When a sufficient

amount of the liquefied gas (enough to insure a permanent layer after the tubes had warmed up) had accumulated, the open end of the tube was sealed off. When the tubes warmed up to room temperature they not infrequently exploded, and such tubes were replaced until full sets were obtained. If a tube was due to explode it usually did so quite promptly on warming up, explosions being quite rare among tubes that had resisted for a few hours.

The reagents used were in all cases four different concentrations of potassium sulphide (10N, N, N/10, and N/100), pure water, and N/10 sulphuric acid. Thus there were six tubes prepared for each mineral.

Observations were carried out on these tubes, beginning immediately after they had warmed up, and thereafter at intervals, the intervals at first being short (a day or two), and later being extended to a week or more. The observations were made by means of a hand lens, goggles also being used as a protection to the eyes.

SUMMARY.

The results of the investigations may be summarized as follows:

1. Hydrogen sulphide is a very powerful mineralizing agent for the four commoner sulphides of copper, namely chalcocite, chalcopyrite, bornite and covellite. Under the influence of high concentrations of this reagent very fundamental changes occur in these minerals at 30°, in periods of time so short as to be easily within the demands of laboratory investigation. The conduct of the minerals in acid solution is quite different from that in alkaline or neutral ones. The main reactions observed may be compiled as follows:

A. In Acid Solutions.

(1) Chalcocite—White—unattacked. Blue—disperses into colloidal and flocculent amorphous material showing no signs of recrystallization.

(2) Chalcopyrite—Sloughs out certain localized impurities.

(3) Bornite—Seems to be a persistent substance, possibly stable.

(4) Covellite—Is stable, showing practically no signs even of recrystallization.

B. In Alkaline Solutions.

(1) Chalcocite—White form is stable. Blue form sloughs off into amorphous material, some going into colloidal solution. Much of this material is re-attracted to the mineral fragment, forming first a sooty layer which afterwards recrystallizes to the white pseudo-hexagonal form. The rate of recrystallization of the white chalcocite is at a maximum in absence of alkaline sulphide, decreases as the alkaline sulphide increases up to a certain point (about normal so far as we have determined) and thereafter increases. The amount of sloughing increases as the concentration of alkaline sulphide increases. The iron present as impurity in all cases combines with some chalcocite to form chalcopyrite.

(2) Chalcopyrite—Is stable and shows only a tendency to sloughing off of localized impurity.

(3) *Bornite*—Breaks down rapidly into covellite, chalcocite and chalcopyrite, all of which are, in a couple of months, obtained in well recrystallized forms. Both the rate of breakdown (as shown by rapidity of sloughing) and the rate of recrystallization seem to be at a maximum in water or faintly alkaline solution.

(4) *Covellite*—Is stable showing only a tendency to recrystallize in thin scales, and this only locally, probably at points of impurity. There is some evidence that seems to indicate under certain conditions the possibility of covellite breaking down into chalcocite and free sulphur, but we prefer to postpone the discussion of this point to a later time.

2. It has been shown that replacements having all the appearance of natural ones may be brought about in the laboratory in comparatively short time. Thus Mr. Beeson found perfect infiltrations of chalcopyrite into veinlets of melaconite in chalcocite, in specimens which we had treated. This would seem to open up a new and interesting method of investigation. Minerals may be sectioned and carefully studied and mapped, then submitted to treatment with various mineralizers and the change noted after repolishing.

American Mineral Wax.

The American need for ozokerite (a substance commonly known as mineral wax) has heretofore been largely met by imports from the mines in Galicia, Austria, but as the war in Europe has seriously affected ocean transportation, interest in the domestic supply of this material has been stimulated. In order to obtain information regarding the deposits of ozokerite in Utah, the principal deposits in this country, a geologist of the U. S. Geological Survey, Department of the Interior, examined, in September, 1914, the deposits near Soldier Summit and Colton, in the central part of the State.

As described in the resulting report by H. M. Robinson, the ozokerite is found in fissures and brecciated zones, principally in the Wasatch formation, of Eocene age. Tests made by the Bureau of Mines on six samples shows their specific gravity, solubility, melting point, and the fractional distillates they yield, and it is suggested that by boiling crude ozokerite with strong denatured alcohol a commercial separation of the refined product ceresin may be made. On account of the irregular distribution of the ozokerite no safe estimate can be made as to the quantity of undeveloped ozokerite, but the quality, as far as the melting point is concerned, compares favorably with the Austrian product and the market conditions brought about by the war in Europe offer exceptional opportunities for the development of Utah ozokerite.

The report of the United States Bureau of the Census on the production of alums in the United States shows that the total output for 1914 was 313,712,000 lbs., valued at \$3,467,969, compared with 276,294,000 lbs., valued at \$3,022,355, in 1909.

THE FLOTATION OF OXIDIZED ORES.*

By O. C. RALSTON and GLEN L. ALLEN.

INTRODUCTION.

Concentration of natural sulphide ores by the flotation process has met with such success that attempts have recently been made to apply the process to the flotation of ores other than natural sulphides.

As inquiries on this subject are frequently received by the Bureau of Mines, it has been thought best to publish a summary of the results so far obtained from the experimental work on oxidized ores at the Salt Lake City station of the bureau, in co-operation with the department of metallurgical research of the University of Utah. The work has been directed by O. C. Ralston, assistant metallurgist of the bureau, and was carried on for the most part by G. L. Allen; N. C. Christensen and R. W. Johnson also assisted with the work.

As above stated, this paper is only a summary, or a preliminary report of the experiments on the flotation of oxidized ores. More complete details as regards the flotation of carbonate ores of lead will be given by the writers in a paper on that subject, and in the near future the bureau expects to publish a still more complete discussion on the flotation of oxidized ores of lead, copper and zinc.

Most of the experimental work in the laboratory at the Utah station has been with the oxidized ores of lead. Only minor attention has been given to the oxidized ores of zinc and of copper for the following reasons: Little success has been had with the zinc ores; many others are engaged in testing copper ores, so that there was no pressing necessity of experimentation with copper ores by the bureau, although an attempt is being made to co-ordinate the work of those who are willing to co-operate to that extent.

SULPHIDIZING AND FLOTATION OF OXIDIZED ORES.

Flotation of oxidized minerals depends upon a preliminary "sulphidizing" by any method that will convert at least the surface of the mineral particles to a sulphide of the metal. This step is followed by flotation of the "artificial" sulphide, which results in a concentration of the metallic values in the low-grade oxidized ore being treated.

The methods of sulphidizing that have been investigated are as follows:

Sulphidizing (1) by the use of hydrogen sulphide on either the dry or the wet crushed ore, (2) by the use of solutions of the various sulphides and sulpho-compounds of sodium, (3) by the use of solutions of the various sulphides and sulpho-compounds of calcium, (4) by the use of sulphur vapor, (5) by the use of a sulphureted oil, (6) with colloidal sulphur.

It has been found that treatment by some of these methods will form a film of sulphide over the surface of the particles of such minerals as lead carbonate or

*Issued by the U. S. Bureau of Mines.

copper carbonate, whereas in other cases the mineral particles are sulphidized to the core. Other methods failed to give any results.

CARBONATE OF LEAD ORES.

All of the above methods of sulphidizing have been tested on a great number of carbonate-of-lead ores. Some of these ores contained silver and some contained lead as the principal metal. A number of the ores have been successfully concentrated and others refuse to yield to concentration by flotation. In general, a high alumina content (acid soluble) in an ore seems to prevent the application of sulphidizing and flotation. The purpose of this report is to give the main features of the flotation of oxidized ores of lead, as well as other ores.

In sulphidizing with hydrogen sulphide gas, as applied to the lead carbonate ores, it was found that the best method of applying the gas to a dry powdered ore was in a tumbling barrel with the gas inlet in the end. Sulphidizing in a glass bottle showed that the ore blackened quickly after the application of the hydrogen sulphide gas. On attempting to float out lead sulphide from the ore as soon as it had blackened it was found that a low extraction of lead was obtained and likewise a low-grade concentrate, unless the pulp was previously acidified with sulphuric acid. By acidifying the pulp, cleaner concentrates were floated but the extractions of lead remained low. Only by prolonged treatment with hydrogen sulphide gas could the extraction of the lead be raised to commercial grade. With a number of ores eight hours' treatment gave an extraction of over 80 per cent of the lead.

The use of hydrogen sulphide was considered for the reason that it can be generated quite cheaply. With iron matte available at \$5 to \$10 per ton, and sulphuric acid at from \$5 to \$10 per ton, the cost of the hydrogen sulphide resulting, including labor, etc., is between \$30 and \$50 per ton. If this gas in combining with the metal in the ore produces only a superficial film of sulphide, and does not penetrate to the center of the particles, it might be possible to make a ton of the gas sulphidize many tons of ore.

Unfortunately hydrogen sulphide attacks the metallic particles of the ore with such avidity that by the time the latter are sulphidized sufficiently to permit of good extraction by flotation, they have also been sulphidized to the core, and practically a chemical equivalent of hydrogen sulphide, to the lead in the ore, has been absorbed. Even coarse pieces of ore in a bottle absorb the gas with evolution of heat, and on breaking open the pieces, the black coloration is seen to have traveled deeply into the particles.

Owing to the fact that the value of the lead concentrate obtained is very low as compared to the amount of hydrogen sulphide necessary to sulphidize it, this process is not regarded as commercially practicable.

Application of hydrogen sulphide to the ground ore suspended in water does not seem to be subject to the same difficulty. True "filming" of the particles with a film of lead sulphide seems to take place, and the extractions possible after a short treatment with the gas are satisfactory. The speed of travel of molecules of hydrogen sulphide gas, as compared with the speed of travel of the same molecules in solution, affords an explanation of the difference in the action of the gas when applied to dry pulverized ore as compared to its action when applied to pulp suspended with water.

The best results on lead carbonate ores have been obtained when sulphides of sodium were used for the sulphidizing agent. The sodium sulphide must necessarily be introduced in solution and seems to cause true filming. The sulphides of sodium considered commercially applicable are the normal sulphide of sodium, Na_2S ; sodium polysulphides, Na_2S_4 and Na_2S_5 , and the sulphhydrate of sodium, NaSH . Of these, the latter, the sulphhydrate, seems to be very effective, as is evidenced by the quicker blackening of the pulp, and the deeper, blacker color formed. The normal sulphide is almost as effective; the polysulphides seem to be the least active. Different ores require 10 minutes to 24 hours of contact with the solutions of sodium sulphide used, depending on the properties of the ore and on the strength of the solution of sodium sulphide. Amounts of sodium sulphide varying from 10 to 20 pounds per ton of ore are usually sufficient, and should be applied to pulp containing about one ton of water per ton of ore, in order that the solution may be as strong as possible during the sulphidizing stage of the process. After a good black color has developed and the color has ceased to increase in blackness, the pulp is diluted with water to a 3:1 or 4:1 mixture and floated in either mechanically agitated or pneumatic machines. The market for sodium sulphide is limited and it should be obtainable at considerably less than 2 cents per pound.

The polysulphide of calcium, obtained by boiling powdered sulphur with slacked lime, seems to be satisfactory for ores that yield easily to sulphidizing, but is sluggish in its action, as compared to the sulphides of sodium. The normal sulphide of calcium is only slightly soluble and hence its use was discontinued as a possible sulphidizing agent. The sulphhydrate of calcium is the most active of these reagents, but has not been tested to any extent in this work, as there is doubt as to whether it would be commercially feasible to prepare such a compound.

Sulphidizing with sulphur vapor has been tried with little success, for the reason that it must be applied at a temperature above the boiling point of sulphur in order to prevent condensation of the sulphur. This means that the ore must be heated to a temperature above 445°C . There seems to be no difficulty in obtaining elemental sulphur vapor commercially, as pyrite will give up half of its sulphur content when heated in a closed space, and sulphur dioxide gas can

be reduced to elemental sulphur by passing it through a heated zone in the presence of a reducing agent. As lead itself is easily reduced from its carbonate form, the temperature might as well be raised to the point where the lead can be liquated out, a reducing atmosphere being used instead of a sulphidizing atmosphere.

The use of a sulphureted flotation oil, in which loosely combined sulphur is available for combination with carbonates of lead or other metals and the rest of the oil is then available for "oiling" the artificial sulphide, has given very little encouragement in the tests conducted by the bureau.

Finally, colloidal sulphur, mentioned as a possible method of sulphidizing, does not seem to combine with lead carbonate at all. It floats as a white lining of the air bubbles in the flotation machine, and brings up very little lead with it.

Usually the precious metals contained in a lead carbonate ore accompany the lead. The writers have noticed that the silver extraction will lag behind the lead extraction when the ore is sulphidized with sodium sulphide, and that the reverse has usually been true when hydrogen sulphide was used.

The importance of sulphidizing flotation is due to the fact that there are many deposits of lead carbonate ore in all of the western States and many of these ores have been milled with varying success. Frequently the lead carbonate can be satisfactorily concentrated by gravity methods, but often it is found that the particles of lead carbonate go into the slimes and are lost. Tailing heaps containing 5 to 10 per cent of lead are common. The object of this investigation is to determine whether sulphidizing flotation could not be applied to the treatment of the deposits of lead carbonate above mentioned, to prevent the waste that now takes place when these ores are treated by gravity concentration processes, and render amenable to treatment carbonate ores that are too low grade to be treated by present methods.

The General Engineering Co., of Salt Lake City, Utah, has carried on extensive tests of different lead carbonate ores with varying success, according to the ore tested. The company owns several sulphidizing patents, which it has either patented or purchased.

A flotation plant to apply sulphidizing and flotation to an ore containing lead, silver and gold is being constructed by the Prince Consolidated Mining Co., at Pioche, Nev., for the treatment of two tailing dumps from former pan-amalgamation and cyanide operations in that vicinity. This plant is expected to be in operation by July 1, 1916.

OXIDIZED COPPER ORES.

Many attempts have been made, both by large operating companies and by other experimenters, to float the carbonate and other oxidized minerals of copper. For that reason the testing of such ores by the writers has been limited.

Hydrogen sulphide seems to be by far the best me-

dium for sulphidizing oxidized copper ores previous to flotation. When applied to the dry ore, the writers found the same conditions as those mentioned for lead; the particles are sulphidized to the center, which requires an excessive amount of hydrogen sulphide. Applied to the wet pulp, the hydrogen sulphide seems to cause true filming. The writers' work has yielded black concentrates, but they are informed by Mr. Callow, of the General Engineering Co., that the company has been able to reduce the amount of sulphur used to a point where the froth is green with slightly coated malachite. He states that as little as one-half pound of sulphur per ton of ore is giving good extractions in the plant of the Magma Copper Co., at Magma, Ariz., where his company has put in the first successful installation of this kind.

Sodium sulphide has been tested by a number of the larger companies who have some oxidized copper minerals in their sulphide ores. The amount of oxidized copper in such ores is usually a fraction of 1 per cent, so that two or three pounds of sodium sulphide per ton of ore are all that is necessary. This is usually added to the machines during flotation, or to the mixing tanks before flotation. The writers' experience is that if some little time of preliminary contact is allowed before flotation is attempted, better sulphidizing of the material will result.

Calcium polysulphide has been used for some time in a number of the large copper concentrating mills with indifferent success, and seems to be detrimental in some instances. On the ores tested by the writers fair results were obtained if the calcium polysulphide was allowed to act until the ore had become well blackened.

It is stated that sulphur vapor was tested at one of the large plants for flotation of oxidized forms of copper and gave better results than any other method of sulphidizing. Of course this method has the disadvantage of having to be applied to dried, heated and finely divided ore.

Sulphureted oils are being used at a number of plants to supplement other methods of sulphidizing and considerable secrecy is observed as to the technical details of this work.

So far as the writers know, colloidal sulphur does not assist in the flotation of oxidized forms of copper. Neither has the silicate of copper been successfully floated by sulphidizing flotation. It will blacken when sulphidized, but resists flotation. Possibly it still presents a silicate surface, rather than a sulphide surface to the flotation elements. For this reason a number of the large copper companies are seriously contemplating leaching the oxidized copper ores, rather than lose what silicate of copper may be present.

Repeated attempts to float the natural sulphides along with sulphidized minerals have failed, as the sulphidizing agents cause trouble with the flotation of the natural sulphides. By careful adjustment this dif-

ficulty has been solved in one plant, though the details are not available.

OXIDIZED ZINC MINERALS.

Attempts to float the oxidized particles of zinc from

TABLE 1.—RESULT OF SULPHIDIZING AND FLOTATION OF OXIDIZED ORES.

LEAD-SILVER ORE.									
Ore No.	Source of ore.	Metal content of ore.		Metal content of concentrate.		Extraction.			
		Lead. Pct.	Silver. Ozs.	Lead. Pct.	Silver. Ozs.	Lead. Pct.	Silver. Pct.		
1	Daly Judge mine, Utah	16.1	20.6	33.6	41.5	83	80		
2	May Day mine, Utah	4.2	2.36	24.6	9.6	80	55		
3	May Day mine, Utah	4.5	2.8	28.4	12.04	86	64		
4	May Day mine, Utah	4.5	2.8	26.1	11.5	73	48		
LEAD ORE.									
		Lead, Per Cent.		Lead, Per Cent.		Lead, Per Cent.			
5	Wilbert Mill dump, Idaho	5.77		28.2			54		
6	Scranton mine, Utah	8.74		65.0			88		
LEAD-SILVER-GOLD ORE.									
		Sil- Lead ver.		Sil- Lead ver.		Sil- Lead ver.		Gold.	
		Pct.	Ozs.	Ozs.	Pct.	Ozs.	Ozs.	Pct.	Pct.
7	Shattuck mine, Ariz. 15.42	12.88	0.05	48.3	45.2	0.128	88	80	70
COPPER-SILVER-GOLD ORE.									
		Copper-Silver per. ver.		Copper-Silver per. ver.		Copper-Silver per. ver.		Gold.	
		Pct.	Ozs.	Ozs.	Pct.	Ozs.	Pct.	Pct.	Pct.
8	Grand Central mine, Utah 0.60	4.80	0.22	4.75	32.9	1.28	67	75	73
ZINC ORE.									
		Zinc, Per Cent.		Zinc, Per Cent.		Zinc, Per Cent.			
9	Honorine mine, Utah	28.45		27.2				Nil	

METHOD OF SULPHIDIZING.

- Ore 1.—Two hours' treatment with H₂S gas on dry ore.
 Ore 2.—Four hours' treatment with H₂S gas on dry ore.
 Ore 3.—Eighteen hours' treatment with 1 per cent solution of Na₂S, 20 pounds per ton of ore.
 Ore 4.—Three hours' treatment with 0.8 per cent solution of CaS, 16 pounds per ton of ore.
 Ore 5.—Four hours' treatment of 1 per cent solution of Na₂S, 20 pounds per ton of ore.
 Ore 6.—One-half hour's treatment with 6 per cent solution of Na₂S, 12 pounds per ton of ore.
 Ore 7.—One-half hour's treatment with 0.75 per cent solution of Na₂S, 15 pounds per ton of ore.
 Ore 8.—Short-time treatment with hot 1 per cent solution of Na₂S, 20 pounds per ton of ore.
 Ore 9.—Na₂S or H₂S in various amounts.

PATENTS ON SULPHIDIZING AND FLOTATION PROCESSES.

A list of patents dealing with methods of sulphidizing and flotation follows:

- U. S. Patent 807,501. Dec. 19, 1905. A. Schwarz.
 U. S. Patent 1,004,760. April 28, 1914. J. T. Terry.
 U. S. Patent 1,008,668. June 2, 1914. H. B. Hovland and G. B. Frankforter.
 U. S. Patent 1,140,865. May 25, 1915. R. F. Bacon.
 U. S. Patent 1,140,866. May 25, 1915. R. F. Bacon.
 U. S. Patent 1,159,942. Nov. 9, 1915. H. B. Hovland.

- U. S. Patent 1,180,816. April 25, 1916. R. F. Bacon.
 British Patent 26,019.* Nov. 10, 1909. H. L. Sulman and H. F. K. Picard.

*Provisional specifications 28,612, Sulman and Picard, applied for Dec. 7, 1909, and 29,616, applied for Dec. 17, 1909, are incorporated in British patent 26,019.

their ores, both before and after sulphidizing by most of the above methods, have met with no success whatever in the laboratory experiments of the writers. They are informed that some headway was made with the problem by Professor Traphagen, at the Colorado School of Mines, but that the sulphide film seemed to come off too easily. However, poor results were obtained, whatever the cause.

The writers' experience has been that most of the carbonate ores of zinc contain important amounts of the silicate, and this may be one reason for the non-success of this work, for the same reasons that copper silicate will not float.

Direct flotation of oxidized minerals of the kind mentioned, so far as known, has not been successfully accomplished. In all of the successful work witnessed by the writers there has been some form of alteration of the oxide to the sulphide. A number of parties claim to be successful in the flotation of copper carbonates without sulphidizing, and others in the flotation of scheelite, fluorite and magnetite. The authors were unable to verify these statements.

RESULTS OF TESTS.

Some of the best results and some average results which have been obtained in the work at the Utah station are given in Table I.

Foreign Trade of the United States.

Exports for the fiscal year ended with June, 1916, amounted to \$4,345,000,000 and the imports were valued at \$2,180,000,000, making a total foreign trade for the year of over \$6,500,000,000, which is much larger than any previous total in the history of American commerce. These figures are announced by the Bureau of Foreign and Domestic Commerce, with the explanation that the figures included for June are an estimate based on the final May statistics.

Thirteen great classes of exported articles yield a total estimated at \$3,024,000,000 for 1916, as against \$1,321,000,000 for all other articles. The following table shows the remarkable increases which have occurred in exports of this group during the last two years:

Classes.	1916.*	1915.	1914.
Iron and steel	\$618,000,000	\$226,000,000	\$251,000,000
Explosives	473,000,000	41,000,000	6,000,000
Raw cotton	370,000,000	376,000,000	610,000,000
Wheat and flour	314,000,000	428,000,000	142,000,000
Meats	270,000,000	206,000,000	143,000,000
Copper manufactures	170,000,000	109,000,000	146,000,000
Mineral oils	165,000,000	134,000,000	152,000,000
Brass and manufactures	126,000,000	21,000,000	7,000,000
Autos and parts	123,000,000	68,000,000	33,000,000
Chemicals, etc.	123,000,000	46,000,000	27,000,000
Cotton manufactures	112,000,000	72,000,000	51,000,000
Refined sugar	80,000,000	26,000,000	2,000,000
Leather	80,000,000	63,000,000	37,000,000

*Estimated upon basis of 11 months.

The total production of the cyanide industry in this country for 1914 was 16,450,225 lbs., valued at \$2,398,674, compared with 13,291,080 lbs., valued at \$1,941,893, in 1909, according to figures reported by the United States Bureau of the Census.

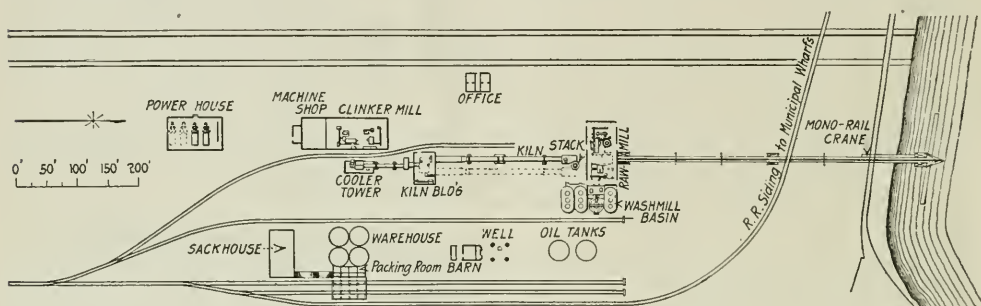
UTILIZATION OF SHELLS IN MANUFACTURE OF PORTLAND CEMENT—PLANT OF TEXAS PORTLAND CEMENT CO.

The extensive shell deposits along the coast of the Gulf of Mexico are now being utilized in the manufacture of Portland cement. The Texas Portland Cement Co. has had a plant in operation at Manchester, Texas, for over two months and during that time has turned over 50,000 bbls. of cement. The wet process for treating the shells, as developed by F. L. Smidth & Co., New York City, is used. The plans for the plant were prepared by H. Struckmann, Kansas City, Mo., consulting engineer for the company, and the actual construction work of the plant was started in the later part of 1915. The following description and illustration of the plant are taken from

basins the chemist gets his first check on the analysis of the raw material before the pumps discharge the finished slurry into a series of storage basins, making it possible to secure a perfect and uniform mix of the raw material before delivering it to the kiln for burning.

This feature in the wet process as used at the Houston plant is one of the important points which has made it practical to produce a high grade and uniform cement out of a material which in the past has had little or no value.

After the finished slurry has been analyzed, corrected and checked, it is delivered to the kiln department ready for the burning process, which takes place in a 9x8x220-ft. rotary kiln operated by variable-speed motors so as to give the chemist perfect control over the burning. Residuum oil is used for fuel.



Layout of Plant of Texas Portland Cement Co.

an article by Mr. Struckmann in the Engineering News.

The plant represents an investment of approximately \$750,000 and as can be seen from the general view the various structures occupy considerable space. Described briefly, it consists of the following buildings and structures.

On the ship channel is a wharf of ample capacity to receive the shell barges, bulkheads having been provided along the shore to prevent any sliding or cave-ins of the bank which might gradually fill up the channel. From the wharf a 650-ft. structural-steel crane runway supports an electrically operated monorail crane, which serves the double purpose of unloading the shells from the barges and delivering them to the mill, as well as delivering the shells from the barges to a 20,000 cu. yd. storage underneath the runway, this precaution being necessary to insure steady operation in the plant whenever weather conditions interfere with the dredging process in Galveston Bay.

Next adjoining the crane structure is the wet raw-grinding department used in treating the shells and clays which are ground preliminarily in a 0.85 wet Kominuter and finished in a 20 tube-mill, discharging the resulting finely pulverized slurry into two basins which are being agitated constantly. From these

From the kiln, the clinkers are discharged into a 6x60-ft. rotary cooler where they are cooled preparatory to adding the usual amount of sulphuric anhydride which is mixed with the clinker in the form of gypsum.

The last stage in the manufacture of the cement, the clinker grinding, is handled with one No. 85 Kominuter and one No. 20 special Danula tube-mill which represents the latest improvement in tube-mill grinding and which has shown a very remarkable saving in horsepower as compared with past known methods of tube-mill grinding.

The product discharged from the clinker mill is delivered to a belt conveyor discharging into the warehouse, which consists of four 30-ft. diameter by 60-ft. high circular concrete tanks nested together, using the ends and interspace for storage in addition to the main tanks.

The packing department, screen house and trainshed are built monolithic with the circular silos, which are elevated to about 4 ft. above the outside ground level so as to permit plenty of air and ventilation in the basement containing the conveying machinery.

The power plant consists of a monolithic concrete structure large enough to accommodate four 450-kw. Diesel engine units, direct-connected to General Elec-

tric generators. Only two of the engines, which were furnished by the Fulton Iron Works, of St. Louis, have been installed for the present capacity, but all arrangements have been made to install two additional units.

In general, the plant has been equipped with the most modern and up-to-date machinery on the market, and it is very gratifying that the wet process has made it possible to treat the material available and produce a high grade Portland cement, incidentally eliminating the usual dust nuisance surrounding a cement plant.

While the plant has now been in successful operation for nearly two months, during which time it has turned out close to 50,000 barrels of cement, the company has just recently started shipments under the direct supervision and recheck of the engineers of the Pittsburgh Testing Laboratory, who certify to the quality of every barrel of cement leaving the plant.

In this connection one of the important features of the plant is that by using oil for fuel and shipping kaolin in from the numerous deposits in Texas, it will be possible to produce pure white cement out of the materials used at Houston.

Production of Chromic Iron Ore.

Chromic iron ore is extensively used in making colors and dyes and refractory materials as well as for alloys in making steel for armor plate, projectiles, and high speed tools, and the demand for it has greatly increased since the war in Europe began.

The chromic ore mines of the Pacific coast have been recently examined by J. S. Diller, of the United States Geological Survey, who reports a remarkable increase in production since the transcontinental railroads have so reduced freight rates as to enable the chrome ore produced on the Pacific coast to compete with the ore imported on the Atlantic border.

For many years California has been the only state producing chromite, and it is still the chief producer. Its production is far greater than ever before. Its output during the first six months of 1916 was more than three times the greatest annual yield of former years and is still increasing. The chief producing areas are the belts of serpentine in the Sierra Nevada and Coast Ranges, which are distributed through a score of counties. Shasta County is still the greatest producer and contains the largest ore body yet discovered in the state.

Nearly all chrome ore is taken out of open quarries. Most of the ore bodies are small and are lenticular in shape, containing from 1 to 200 long tons of ore. Few contain as much as a thousand long tons of ore, and many are the source of blasted hopes in those who exploit them with great expectations.

Bodies of chrome ore have recently been discovered in different parts of Oregon, where production has already begun. The development of some promising bodies is awaited with much interest.

FORTHCOMING MEETINGS OF AMERICAN CHEMICAL SOCIETY AND ASSOCIATED BODIES.

Official announcement of the meeting of the American Chemical Society, to be held in New York, Sept. 25 to 30, in conjunction with the Second National Exposition of Chemical Industries, was issued to the members by Dr. Charles L. Parsons, secretary, on Aug. 15. Dr. Charles H. Herty, of the University of North Carolina, president of the American Chemical Society, will open the exposition on Monday, Sept. 25, at 2 o'clock in the afternoon, with an address reviewing the history of chemistry and the chemical industries in this country and outlining developments since the outbreak of war in Europe. The presidents of co-operating societies, such as the American Electrochemical Society, the American Institute of Mining Engineers and the American Paper and Pulp Association will follow Dr. Herty with speeches of welcome and reviewing the progress made in the industries represented by them.

The first general session of the American Chemical Society will open at Columbia University on Tuesday morning, Sept. 26, and arrangements are being perfected for a public meeting in the large hall of the College of the City of New York on Tuesday afternoon, when addresses will be made of general public interest pertaining to the interesting developments in the field of applied chemistry during recent years.

The program of the week's meeting will provide for general conferences on subjects in which the chemists of the country are now interested and it is intended that the lecture hall of the Grand Central Palace and Rumford Hall in the Chemists' Club building will be occupied each afternoon at the same time by one or other of the different divisions of the society for the discussion of such industrial topics as the production of dyestuffs, medicinal chemicals, industrial alcohol, the manufacture of paper pulp and by-products, oils and motor fuels, glassware and porcelain, steel alloy metals, new developments in chemical industries, etc.

On Wednesday and Thursday mornings a general symposium on colloids will be held, theoretical considerations being discussed on the first day and the industrial applications of colloid chemistry on the second day.

The American Electrochemical Society has planned a series of interesting meetings. The electrochemical group will open its meeting later in the week, on Thursday, Sept. 28, with a technical session devoted to a review of American progress in the electrochemical industry. A complimentary smoker will be held on Thursday evening and on Friday evening there will be a joint banquet at the Waldorf-Astoria of the members of the American Chemical Society, the American Electrochemical Society, and the Technical Association of the Pulp and Paper Industry. This will be a subscription banquet.

THE DETERMINATION OF SULPHURIC ANHYDRID IN PORTLAND CEMENT ANALYSIS.

By EDWIN G. PIERCE, M. Sc.*

While chemical engineers in our Portland cement mills are making various improvements in the process, and in methods of grinding, conveying, handling, etc., they have apparently neglected opportunities for more efficient work in their own laboratories.

To carry out an operation in six hours when only four are required, may involve as great an error in efficiency as to carry out financial calculations to the fourth decimal place. The efficient chemist must determine the degree of precision which his process requires and seek the shortest method that will give uniform results of the required accuracy.

Many of the analytical methods authorized for cement were worked out to secure the greatest possible accuracy and to follow them religiously in routine and control work where such precision is of no value is a serious mistake when shorter methods giving sufficient accuracy are available.

The writer has already pointed out¹ that for years we have used every hour of the day, an unnecessary piece of apparatus, viz.: the reflux condenser in the Newberry or acid and alkali lime determination, with much loss of time.

During the past year the writer has turned out the daily cement analysis, except the magnesia, in four hours while doing his share of the other routine work as well. This shorter method was developed after careful observation of the sources of error in the analysis and their several effects upon the final results. These analyses check those by longer methods well within the limits of error. However, it is the purpose of this paper to describe but one phase of this short method, viz: the determination of sulphuric anhydrid.

The experience of having several sulphates which had stood over night pass repeatedly through the filter, led to a series of observations and experiments, and to the habit of saving the filtrates. These each standing for varying periods, usually over night, and stirred with a centrifugal motion, always showed some precipitate collecting in the center, indicating that the determination as ordinarily carried out with commercial papers is, at best, only approximately correct. Various papers and changes in the method were tried, but always some sulphate would appear in the filtrate. Next, the filtrate was collected in three portions, viz.: (1) the supernatant liquid, (2) the filtrate secured while bringing the precipitate upon the paper, (3) the wash water. In nearly all cases, less precipitate appeared in 1 than in 2 and 3 showing that precipitation was complete but the sulphate was carried

through the paper mechanically. Efforts to study the situation from the standpoint of colloidal chemistry resulted in the conclusion that the precipitate is not a true colloid but may contain many very small crystals. However, information secured from this study furnishes the basis for the method to be described.

According to the colloid theory of P. P. von Weimarn,² particles of colloidal solutions are all crystalline, and the magnitude of the crystals depends upon the concentration, pressure, and temperature condition, decreasing with dilution.

Ostwald³ points out that small crystals are more soluble than large ones, hence when both are present there will be a condition of supersaturation for larger crystals causing them to grow, and of hypersaturation for small crystals causing them to dissolve. High temperatures also increase this solubility.



Zsigmondy states⁴ that the crystalloid solubility of barium sulphate is too great to permit the preparation of a colloid.

Lehmann in explaining the process of crystal growth gives the following: When a precipitant is added to a solution at a given point causing crystals to form, the solution becomes impoverished at that point, tending to the formation of small ones. The growth of crystals is aided by diffusion currents in the liquid by which fresh material is brought in contact with the nucleus. Secondary and tertiary lines of growth shoot off from the parent stems thus exposing greater surface to diffusion currents, and causing the skeletal outline to fill up. Growth is retarded by the presence of layers of different temperatures in the solution which effect pressure and solubilities.

From the above considerations it is evident that to suppress the formation of small crystals and assist the formation of large crystals at the outset, and to foster the growth of these large crystals at the expense of

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¹Journ. of Ind. & Eng. Chem., Vol. 7, No. 3.

²Arbeiten Weimarn.

³Lehrbuch d. allg. Chemie, 2-757.

⁴Colloids and the Ultramicroscope.

the small ones will add to the completeness of the BaSO_4 separation.

To provide an even distribution of heat throughout the solution, prevent "bumping," diffuse the precipitant rapidly, and constantly reduce the volume of the solution: boiling tubes are used as shown in the illustration. These consist of a capillary tube attached to a stem of convenient length, and give a steady flow of bubbles from the bottom which prevents superheating, and boiling may be continued without attention as long as desired. The boiling BaCl_2 solution is added very slowly, allowing rapid diffusion and boiling is continued till the BaSO_4 settles to the bottom. The tube is then removed with a quick jerk while boiling continues so that no liquid will be drawn into the capillary, and the beaker placed on a sand bath or hot plate kept just below the boiling point and allowed to stand about two hours. The solution is then rapidly cooled with running water and filtered. From theoretical considerations already mentioned it is evident that a slow paper is preferable, as there will be less suction and less sulphate drawn through while bringing the precipitate upon the paper. The larger crystals and skeletal forms will clog the pores and hold

perfectly white to constant weight at 925°C . in twenty to thirty minutes.

Specifications for cement analysis usually require that the BaSO_4 shall stand five hours before filtering and the determination covers about seven hours. The above method will give the same result within the limits of error, and allow the analyst to complete a determination in a half day; e. g., if the precipitation is complete at 8:30 A. M., the sulphate can be filtered between 10:30 and 11:00 leaving ample time for ignition, cooling and weighing before noon.

Whatever period of standing is allowed, the boiling tubes will be found a distinct advantage: they are also useful in boiling down lime filtrates for the MgO determination.

For greater precision in the barium sulphate determination, the excellent paper of P. P. von Weimarn⁵ gives valuable hints.

The Table I gives a comparison of results.

Pulp and Paper Prices in Norway.

According to a recent issue of the Tidsskrift for Papirindustrie, Norwegian pulp prices continue to soar and the United Kingdom pays fancy prices for the odd lots available of this year's production. Bleached sulphite is quoted at \$186.67 per long ton, easy bleach at \$160 to \$173.33, strong at \$146.67 to \$160, and kraft soda at \$133.33, net cash to makers, f. o. b. Norwegian ports. In Sweden prices keep about \$67 lower. The United States continues to keep back from the market, but Sweden claims to be receiving sufficient orders from Germany.

Dry mechanical pulp is firm and scarce at \$40 to \$41.33 f. o. b. per ton, while that which is 50 per cent moist has advanced. The current value today is \$14.67 to \$17.33 per ton, f. o. b. Norway. The demand is good, but the stocks are small. Baltic mechanical pulp mills seem to be working at full pressure, as it is understood that 40,000 tons for prompt delivery have been taken up by the German market at about \$8 f. o. b. per ton.

For the first time in several months the paper market is not rising. There is now actually a stagnation in prices, and the market on the whole is a little easier. There may be several reasons for this, but it is believed that it is partly due to the fact that France does not pay the prices lately demanded. The French newspapers have formed a buying syndicate, and it is said, too, that Scandinavian prices are again considerably higher than those demanded by Canadians. A few varieties other than newsprint, such as grease proofs, are also a little easier, whereas better-class papers are almost unobtainable. Mills making paper for the Chinese market are in an awkward position on account of the shortage of tonnage. Large lots of paper booked for March and April shipment have not been forwarded by the steamship lines, owing to lack of room; thus the stocks of the mills are large. Relief, however, is in sight.

TABLE I.— SO_4 DETERMINATIONS.

Sample.	Boiling tubes.	Time of standing, hours.	Residue from supernatant liquid.	Residue from washing beaker.	Residue in wash water.	Number of washings.	SO_4 per cent.
1.....	Not used	36	Trace	1	1	1	1.46
2.....	Not used	42	Trace	1	1	1	1.46
3.....	Used	24	Trace	1	1	1	1.46
4.....	Not used	36	Trace	1	1	1	1.46
5.....	Not used	36	Trace	1	1	1	1.46
6.....	Used	24	Trace	1	1	1	1.46
7.....	Not used	36	Trace	1	1	1	1.46
8.....	Not used	36	Trace	1	1	1	1.46
9.....	Used	24	Trace	1	1	1	1.46
10.....	Not used	36	Trace	1	1	1	1.46
11.....	Not used	36	Trace	1	1	1	1.46
12.....	Used	24	Trace	1	1	1	1.46
13.....	Not used	36	Trace	1	1	1	1.46
14.....	Not used	36	Trace	1	1	1	1.46
15.....	Used	24	Trace	1	1	1	1.46
16.....	Not used	36	Trace	1	1	1	1.46
17.....	Not used	36	Trace	1	1	1	1.46
18.....	Used	24	Trace	1	1	1	1.46
19.....	Not used	36	Trace	1	1	1	1.46
20.....	Not used	36	Trace	1	1	1	1.46
21.....	Used	24	Trace	1	1	1	1.46
22.....	Not used	36	Trace	1	1	1	1.46
23.....	Not used	36	Trace	1	1	1	1.46
24.....	Used	24	Trace	1	1	1	1.46
25.....	Not used	36	Trace	1	1	1	1.46
26.....	Not used	36	Trace	1	1	1	1.46
27.....	Used	24	Trace	1	1	1	1.46
28.....	Not used	36	Trace	1	1	1	1.46
29.....	Not used	36	Trace	1	1	1	1.46
30.....	Used	24	Trace	1	1	1	1.46
31.....	Not used	36	Trace	1	1	1	1.46
32.....	Not used	36	Trace	1	1	1	1.46
33.....	Used	24	Trace	1	1	1	1.46
34.....	Not used	36	Trace	1	1	1	1.46
35.....	Not used	36	Trace	1	1	1	1.46
36.....	Used	24	Trace	1	1	1	1.46
37.....	Not used	36	Trace	1	1	1	1.46
38.....	Not used	36	Trace	1	1	1	1.46
39.....	Used	24	Trace	1	1	1	1.46
40.....	Not used	36	Trace	1	1	1	1.46
41.....	Not used	36	Trace	1	1	1	1.46
42.....	Used	24	Trace	1	1	1	1.46
43.....	Not used	36	Trace	1	1	1	1.46
44.....	Not used	36	Trace	1	1	1	1.46
45.....	Used	24	Trace	1	1	1	1.46
46.....	Not used	36	Trace	1	1	1	1.46
47.....	Not used	36	Trace	1	1	1	1.46
48.....	Used	24	Trace	1	1	1	1.46
49.....	Not used	36	Trace	1	1	1	1.46
50.....	Not used	36	Trace	1	1	1	1.46
51.....	Used	24	Trace	1	1	1	1.46
52.....	Not used	36	Trace	1	1	1	1.46
53.....	Not used	36	Trace	1	1	1	1.46
54.....	Used	24	Trace	1	1	1	1.46
55.....	Not used	36	Trace	1	1	1	1.46
56.....	Not used	36	Trace	1	1	1	1.46
57.....	Used	24	Trace	1	1	1	1.46
58.....	Not used	36	Trace	1	1	1	1.46
59.....	Not used	36	Trace	1	1	1	1.46
60.....	Used	24	Trace	1	1	1	1.46
61.....	Not used	36	Trace	1	1	1	1.46
62.....	Not used	36	Trace	1	1	1	1.46
63.....	Used	24	Trace	1	1	1	1.46
64.....	Not used	36	Trace	1	1	1	1.46
65.....	Not used	36	Trace	1	1	1	1.46
66.....	Used	24	Trace	1	1	1	1.46
67.....	Not used	36	Trace	1	1	1	1.46
68.....	Not used	36	Trace	1	1	1	1.46
69.....	Used	24	Trace	1	1	1	1.46
70.....	Not used	36	Trace	1	1	1	1.46
71.....	Not used	36	Trace	1	1	1	1.46
72.....	Used	24	Trace	1	1	1	1.46
73.....	Not used	36	Trace	1	1	1	1.46
74.....	Not used	36	Trace	1	1	1	1.46
75.....	Used	24	Trace	1	1	1	1.46
76.....	Not used	36	Trace	1	1	1	1.46
77.....	Not used	36	Trace	1	1	1	1.46
78.....	Used	24	Trace	1	1	1	1.46
79.....	Not used	36	Trace	1	1	1	1.46
80.....	Not used	36	Trace	1	1	1	1.46
81.....	Used	24	Trace	1	1	1	1.46
82.....	Not used	36	Trace	1	1	1	1.46
83.....	Not used	36	Trace	1	1	1	1.46
84.....	Used	24	Trace	1	1	1	1.46
85.....	Not used	36	Trace	1	1	1	1.46
86.....	Not used	36	Trace	1	1	1	1.46
87.....	Used	24	Trace	1	1	1	1.46
88.....	Not used	36	Trace	1	1	1	1.46
89.....	Not used	36	Trace	1	1	1	1.46
90.....	Used	24	Trace	1	1	1	1.46
91.....	Not used	36	Trace	1	1	1	1.46
92.....	Not used	36	Trace	1	1	1	1.46
93.....	Used	24	Trace	1	1	1	1.46
94.....	Not used	36	Trace	1	1	1	1.46
95.....	Not used	36	Trace	1	1	1	1.46
96.....	Used	24	Trace	1	1	1	1.46
97.....	Not used	36	Trace	1	1	1	1.46
98.....	Not used	36	Trace	1	1	1	1.46
99.....	Used	24	Trace	1	1	1	1.46
100.....	Not used	36	Trace	1	1	1	1.46

back the smaller crystals but some particles of small size pass through before this takes place as shown by examination of the filtrate. For the same reason it is best in washing not to disturb the mat of crystals first formed on the paper but merely circle the top with the stream from the wash bottle, since by more violent washing there is a greater loss of small particles. In bringing the precipitate upon the paper there can be no advantage in any extensive washing and swabbing of the beaker to remove last traces of BaSO_4 since each additional washing carries more small particles through the paper than will be removed from the beaker. If the precipitation has been properly carried out and the BaSO_4 settled out perfectly clear, it can be brought upon the paper and the beaker sufficiently rinsed in three applications of the wash bottle, and with three additional washings of the paper the filtrate will show barely a trace of chlorides. The writer uses double papers which require about three to five minutes to drain and gives about twenty minutes for filtration—accomplished while doing other work. The precipitate secured in this way will ash

⁵Grundzüge der Dispersoid Chemie.

ELECTROLYTIC CHLORINE FOR LAUNDRIES.*

By H. P. HILL.

For several years a number of the larger laundries have prepared their own bleaching material by the electrolysis of salt solution, finding it cheaper to produce their own "bleach" than to purchase the bleaching compounds which were largely manufactured abroad and exported to this country. In recent months, however, the sharp advance in the prices of bleaching compounds of all kinds has made it increasingly desirable for even smaller laundries to produce their own chlorine solutions by the electrolysis of salt and water.

The electrolytic load thus afforded the central station is comparatively long-hour in character, and may be arranged so as to fall entirely during the daylight hours. In the following paragraphs are given descrip-

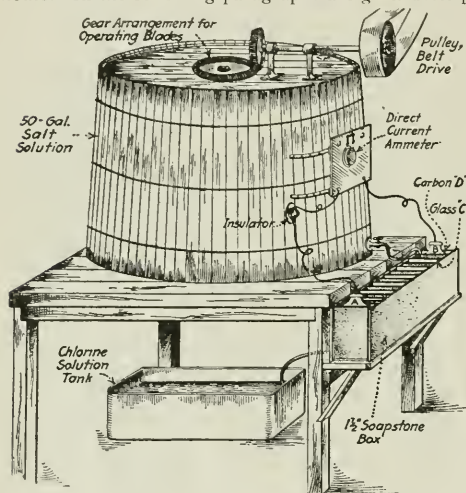


Fig. 1—Electrolytic Chlorine Tank for Producing Bleaching Solution from Salt and Water.

tions of typical equipment for the production of chlorine for laundries and other industries, including the reclamation of tin from old cans.

CONSTRUCTION OF 50-GAL. OUTFIT.

Fig. 1 shows a 50-gallon outfit, which requires 25 amp. of direct current at 110 volts. The equipment, as shown in the sketch, comprises a 50-gallon wood tub mounted on a stand 3 ft. above the floor, and filled with a solution of common salt and water. In the center of the tub is a shaft on which is mounted a blade or paddle which slowly revolves in the tub to agitate and dissolve the salt. On the side of the tube is mounted a soapstone box containing the electrodes. This box measures 22 in. long, 9 in. wide and 6 in. deep. At each end are placed the carbon-block electrodes *A* and *B*, and spaced at 3-in. intervals are alternate glass and carbon plates *C* and *D*. Each plate has

a 1-in. square "bite" taken out of one corner. The object of these baffles or plates is to diminish the flow and keep the solution in contact with the current, through a longer path. The salt water from the tub is admitted at the negative element, and is discharged at the positive element. From the discharge end chlorine solution flows into a tub on the floor, from which it is dipped and used in the washing machine. This solution is known as "chick" or bleaching compound.

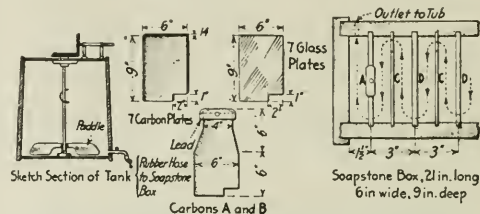


Fig. 2—Details of Tank and Electrolytic Chamber.

The form of apparatus just described can be improved in efficiency by modifying the design of the soapstone box, as shown in Fig. 3. The top of the box shown in this sketch is covered, and the chlorine gas generated instead of being allowed to escape in the air is piped to the bottom of the salt tub, or can be carried in pipes to a bleaching or drying room, where it is of value. Another advantage of confining the chlorine gas as in Fig. 3, by closing the top of the salt tank, is that the amount of the gas given off will

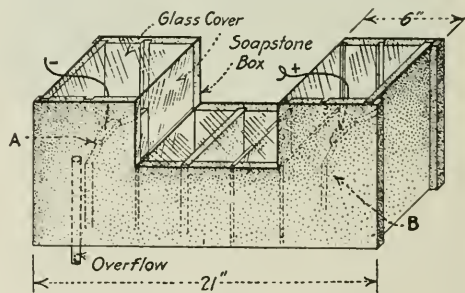


Fig. 3—Closed Electrolytic Chamber for Collecting Chlorine Gas.

determine the feed or overflow of the chlorine discharge from the positive side of the box, and insure a solution of maximum strength at all times.

OTHER USES FOR CHLORINE PRODUCTS.

Another use for this form of apparatus is that of removing the tin from old cans, etc. A brick retort is built with proper means of heating the metal up to the proper temperature, and the solution of chlorine gas coming in contact with the heated metal attacks the tin.

A novel form of a chlorine generator used as a disinfectant or purifier is shown in Fig. 4. In this type the apparatus is automatic and the current automatically cuts itself off when a supply of chlorine is made.

*From Electrical World.

The outfit can be adjusted to feed as little gas as reckoned for a single concern was large, but naturally quired, the supply and discharge being regulated by the gas pressure in the generator. The bottle, usually 1 gallon in size, is filled with a saturated solution of salt water, and is inverted over the glass or earthenware crock, which a gasket makes airtight. The glass tube extends to within approximately 1 in. of the bottom of the crock.

FOR MAKING CHLORINE IN SMALL QUANTITIES.

The tube measures 3 in. in diameter and is sealed into the top so as to be gastight. On an iron rod is clamped the positive carbon, which is connected in series with a 32-cp. incandescent lamp. In the U-bend discharge pipe is a valve which is adjusted for the proper discharge. When the bottle is filled with the saturated salt solution, and the current is turned on,

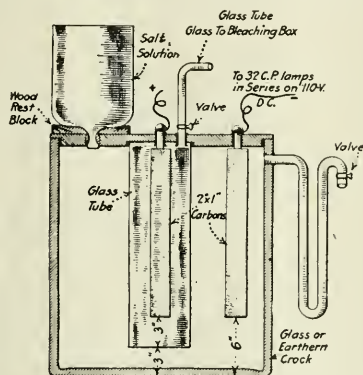


Fig. 4—Apparatus for Producing Chlorine in Small Quantities.

chlorine gas is formed inside the 3-in. glass tube. This gas drives the solution down in the tube until the circuit is interrupted at the bottom of the electrode. If the valve in the outlet pipe is closed or set for a small discharge this gas will condense, and allow the solution to rise in the tube, re-establishing the circuit and so generating more chlorine. As the chlorine is discharged through the U-tube new solution is allowed to feed down from the bottle, and the apparatus automatically makes the amount of chlorine within its capacity as required. A glass tube can be extended through the cover into the large glass tube, obtaining directly a supply of chlorine gas for bleaching purposes. This apparatus provides a ready means of securing chlorine solution or chlorine gas in small quantities at little expense. It has a wide field as a disinfectant or purifier and is applicable to many industrial uses.

The Department of Agriculture in its report of August 1 cuts its cotton crop estimate of June 25 by 1,300,000 bales. The report places the condition of the crop on July 25 at 72.3 per cent of normal and indicated a total production of 12,916,000 bales.

COMMERCIAL FERTILIZERS IN GERMANY.

A review of Germany's manufacture of commercial fertilizers since the outbreak of the war and the consequent interruption of imports of Chilean saltpeter, appeared recently in the Frankfurter Zeitung. The following translation of the article is taken from the Daily Commerce Report.

Potash salts in whatever quantities desired are at Germany's disposal through large native deposits, but for nitrogen fertilizers the country was dependent upon Chilean saltpeter, except for such supplies as were obtained through plants which assimilate nitrogen and from natural manures. The imports of Chilean saltpeter have increased rapidly in recent years, although 1913 fell somewhat behind 1912 in both quantity and value, as the following table shows:

Year.	Tons.	Value.
1890	344,209	\$13,107,375
1900	486,115	18,511,165
1910	749,945	31,770,620
1911	730,939	32,183,310
1912	812,898	42,563,445
1913	774,318	40,911,960

Ammonium sulphate obtained as a by-product from coke ovens, and to a less extent from gas plants, has in recent years partly taken the place of Chilean saltpeter. Ammonium sulphate was for a time imported from Great Britain, but has lately become an article of much commercial importance in Germany with a considerable export as well as import trade. The total domestic output in recent years is stated to have been: 1900, 104,000 tons; 1909, 281,000 tons; 1910, 313,000 tons; 1911, 418,000 tons; 1913, 501,000 tons. Exports for 1910, 1911 and 1913 exceeded imports by almost 50,000 tons a year.

In 1913 it is said 460,000 tons of ammonium sulphate were used for fertilizer purposes as against about 750,000 tons of Chilean saltpeter. Reckoning the fertilizer value of ammonium sulphate as compared with Chilean saltpeter at 4 to 3, the first-named product would be equivalent to 610,000 tons of the latter, showing that the two articles had become close rivals in Germany.

In 1914 synthetic ammonium sulphate came into competition in a practical way with Chilean saltpeter. The possibility of producing ammonia synthetically had long been known and had played an important role in chemical literature. For a time the well-known Norwegian process was carried out in large factories in which the German chemical industry was interested, the scarcity of water power making it difficult to carry on this manufacture in Germany. When later the Badische Anilin und Sodafabrik, working in conjunction with Prof. Haber, discovered an extraordinarily satisfactory and epoch-making process for obtaining the product, connection with the Norwegian plants was severed and efforts were centered upon the Haber process. By the time war broke out the total output

did not approach a quantity sufficient, even when added to other nitrogen compounds, to offset the imports of Chilean saltpeter. As a result during the first year of the war there was a scarcity of fertilizers, which was made the more acute by the heavy demands of the military authorities.

Manufacture promptly adjusted itself to the new demand, however, and would now be able, if need be, to furnish larger supplies than are required in time of peace. Under the Haber process the output for 1913 was approximately 30,000 tons, which in 1914 was increased to 60,000 tons, and by the middle of 1915 the capacity of the original factory was 150,000 tons, while for 1916 the estimated output will be 300,000 tons. It is said to be no secret that the Badische Anilin und Sodafabrik is now erecting large additional factories and that as a result the output by 1917 will greatly exceed the present production. Assuming that 500,000 tons of nitrogen fertilizers can be produced by the Haber process annually, it will be seen that this total approaches that of the former Chilean saltpeter imports. Reckoned on the basis of \$60 per ton, this would mean a yearly business of about \$30,000,000. Through other processes, assisted by governmental aid, large supplies of nitrogen were obtained in forms available for agriculture, so that the country is at present secure so far as fertilizers are concerned.

Recent developments in the German coal industry indicate that more and more the tendency will be to utilize by-products. Unless all signs fail, in the near future the direct burning of coal will be looked upon as wholly uneconomical. This will mean increasing many times the production of ammonia from coal. Assuming that the by-products were saved from double the amount of coal now so utilized, there would be a further gain of around 450,000 tons of ammonia, and German agriculture, without any imports of Chilean saltpeter, would have at its disposal more nitrogen fertilizers than before the war. Taking together the three native sources of nitrogen, namely, ammonia from coke, ammonia from the Haber process, and nitrates of lime, the total output of which is not definitely known at present, and comparing them with the like products available in 1913, the results are approximately as follows:

Fertilizers.	Tons.	Nitrogen equivalent, tons.
Consumption, 1913—		
Sulphate of ammonia.....	460,000	92,000
Norwegian saltpeter	35,000	4,500
Nitrate of lime	30,000	6,000
Ammonia, Haber process	20,000	4,000
Chilean saltpeter	750,000	116,000
Total nitrogen		222,500
Production, 1917—		
Sulphate of ammonia	700,000	140,000
Nitrate of lime	400,000	80,000
Ammonia, Haber process	500,000	100,000
Total nitrogen		320,000

COMMENTS ON THE KREBITZ PROCESS OF SOAPMAKING AND GLYCEROL RECOVERY.*

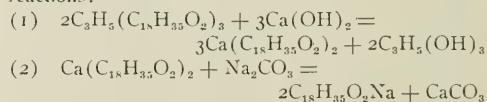
By G. A. WRISLEY.†

The process of soapmaking by boiling fats and oils (glycerides) with caustic soda is, in general, considered the most practical process since it yields soaps of uniformly good quality, color and hardness, and at the same time a good amount of glycerol may be recovered by comparatively simple means. The yield of glycerol from the soap lye runs from 60 to 80 per cent of the total amount formed by the saponification of the fats and oils. The loss depends upon the few or many washes that the soap receives. However, it seems that no matter how careful one is to make the washes and changes on the soap, there is always some glycerol, $\frac{1}{2}$ to 1 per cent, left in the soap. It has also been demonstrated that in evaporating down waste lyes and handling so much salt which cannot be perfectly dried and freed from glycerol, that there is recovered but about 90 per cent of the glycerol that is in the soap lye. Hence, even after the glycerol is in the soap lye, there is a loss in its recovery.

With the continually advancing price of fats, oils and other raw materials, it is becoming more necessary for the soap manufacturer to obtain a large glycerol yield; in fact, it is essential that he should recover all the glycerol liberated by the saponification. Then, too, the grade of fats and oils obtainable for soapmaking is lower, because of increased utilization of the better grades for edible purposes, so that the soap manufacturer must strive to produce a good quality soap from a poorer grade of material.

The Krebitz process, here discussed, offers the possibility of recovering the theoretical yield of glycerol, while at the same time the caustic lime exercises some purifying action, especially in the case of a low-grade material. The Allen B. Wisley Company, of Chicago, is the first in this country to work this process on a large scale with good results.

The Krebitz process is based on two simple chemical reactions:



In practice a batch of 10,000 pounds of fat and oil may be conveniently handled. In a rather shallow tank 1,200 to 1,400 pounds of lime are slaked with 3,700 to 4,500 pounds of water, and the mass is heated, if necessary, to about 70° C. Then the fat and oil are run in while the entire mass is stirred vigorously. With live steam the mass is heated up slowly to 90-92° C., and taking about one-half hour to gain that tempera-

*From the Journal of the Industrial and Engineering Chemistry. The paper was presented before the 52d Meeting of the American Chemical Society, Urbana-Champaign, April 13-21, 1916.

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ture, with constant stirring, a thorough emulsion is obtained. The vessel is then covered to prevent loss of heat. Two or three hours after covering, the mass is likely to boil and swell considerably. After it has stood 8 to 12 hours, it has the appearance of a solid porous mass which is still sufficiently warm and soft to allow digging out the lime soap. This lime soap is dropped through a trap door in the bottom of the tank into a hopper and then to the mill, where it is ground to the size of fine corn meal.

With the lime and water there will result between 15,000 and 16,000 pounds of lime soap from 10,000 pounds of fat and oil. The finely ground soap is carried on a conveyor and allowed to fall loosely into a circular, hopper-shaped tower, a capacity of about 25,000-30,000 pounds being necessary. Four washes, about 40,000 pounds of water, are required to leach out the glycerol from such a batch. The first wash water contains 10 to 12 per cent of glycerol, and is sent to the glycerin works. The second, third and fourth waters are put on a fresh batch, only the last wash being made with fresh water. In this way there is no cause for evaporating glycerin water containing less than 10 per cent of glycerol. When the plant is working satisfactorily, the water evaporated averages 15 per cent of glycerol.

After the glycerol has been obtained, the lime soap is carried by a conveyor and introduced slowly into the soap kettle containing a boiling solution of soda ash. After the lime has been replaced by the soda, a stage which can be noticed by the nonappearance of small lumps on the paddle, a small amount of caustic soda is added, and shortly after the soap is salted out. The contents of the kettle are allowed to rest, when CaCO_3 settles out at the bottom as a heavy sludge, and the soap gathers on top, a salt solution containing an excess of alkali forming an intermediate layer.

Although Krebitz claims that the lime sludge will settle out and occlude or entangle but 4 to 7 per cent of soap, it has been impossible, so far, to prevent the occlusion of less than 9 to 12 per cent of soap. Of course, this soap must be recovered. At first this constituted quite a serious problem, because the lime sludge could not be filtered without leaving 2 to 3 per cent of soap in the lime cake. Attempts to wash out the soap by a series of washings and filtration were unsuccessful, because so much soap was present as to fill up the pores of the filter cloth, making filtration slow and unsatisfactory. Attempts to boil up the sludge with a little water and resalt out the soap were unsuccessful, because on salting out, the lime sludge settled to the bottom, carrying most of the soap with it again. By continued experiment, it was found that the addition of enough water with heat and vigorous agitation caused the soap to go into solution, and on allowing the mass to settle the lime sludge, occluding but 3 to 5 per cent of soap, went to the bottom, the soap rose to the top, and could be pumped off and so recovered. The lime sludge could then be easily

filtered, and only 1 to 1.5 per cent of soap is lost in the lime cake. This loss, though small, may perhaps still be reduced.

The quality and color of the finished soap obtained by the Krebitz process compares favorably with the soap produced by any other process. The amount of lime found in the finished soap depends on the number of washes or changes made in the kettle. Usually there was never less than 0.2 per cent of lime and it may run as high as 0.5 to 0.7 per cent lime. The process, however, claims that only a few thousandths of 1 per cent should remain in the finished soap.

At the present time a yield of about 95 per cent glycerol is being obtained by this process. This, compared to the yield of 60 to 80 per cent obtained by the recovery of glycerol from the soap lye in the case of soapmaking by boiling the glycerides with caustic soda, would give the Krebitz process a decided advantage. Moreover, we must recall that soap lyes contain at best but 5 to 8 per cent glycerol, depending on the way in which the changes of soap lye are worked up, and at the same time hold in solution much common salt, some caustic soda, soda ash, and organic impurities; whereas the Krebitz waters contain 12 to 15 per cent glycerol and are comparatively free from impurities, thereby making purification more simple and giving less water to handle and evaporate. Soda ash is cheaper than caustic soda, and since soda ash is used in place of caustic soda, another material saving is made.

Without doubt, the Krebitz process would be preferred at this time, because of the high price of glycerol, but were glycerol 15 to 20 cents per pound instead of 55 to 60 cents per pound, there might be a shadow of doubt as to whether it would be preferred to the soap-lye process, taking into consideration the manifold operations prior to the soapmaking proper, and the work necessary to recover all the entangled soap from the lime sludge.

Manufacture of Wool Shoddy in United States.

A summary of the general results of the 1914 study of the wool-shoddy industry in this country has been issued by the United States Bureau of the Census. The total value of products in 1914 was \$7,706,843, an increase of 12.4 per cent over the 1909 figure, \$6,854,993. More than three-fourths of the 1914 total represented the value of recovered wool fiber, of which the production in that year amounted to 43,156,037 pounds, valued at \$5,977,284.

The principal materials used in the wool-shoddy industry are rags, tailor's clippings, etc., of which there were consumed in 1914, 57,367,962 pounds, at a cost of \$3,103,864, representing an increase of 32.5 per cent in quantity and 17.4 per cent in cost, compared with the consumption in 1909—43,296,261 pounds, costing \$2,644,570. In addition 6,879,366 pounds of noils and waste, at a cost of \$863,633, were consumed in 1914.

BASIC PHOSPHATE FERTILIZER AS A BY-PRODUCT IN IRON SMELTING.

A practical method of manufacturing phosphate fertilizer from open hearth slag has been devised by the Tennessee Coal, Iron & R. R. Co., one of the subsidiaries of the U. S. Steel Corporation. The following description of this method is reprinted from an article by Mr. H. H. Estep in *The American Fertilizer*:

The fertilizer manufactured by the Tennessee Company is known as duplex basic phosphate. It is a finely ground phosphatic fertilizer manufactured from a slag produced in the open-hearth furnace in connection with the duplex—or, more accurately speaking, the triplex—process of manufactured steel. To carry out this process successfully it has been found necessary to give as much attention to the production of a slag that will be suitable for fertilizer as to turn out steel of a satisfactory quality. The crude slag obtained from the furnace is ground in a series of mills to such a fineness that 80 per cent will pass a 100-mesh screen. This finely ground slag, as prepared for market, contains a minimum of 19 per cent phosphoric acid and 45 per cent lime. Phosphorus, as is well known in agricultural circles, is an essential element of plant food. From 80 to 90 per cent of the phosphoric acid is soluble in a 2 per cent solution of citric acid, and therefore is readily available as a plant food; the remaining 10 to 20 per cent is held in the soil and later becomes available.

Besides phosphorus and lime, duplex basic phosphate contains 6 to 9 per cent of magnesia, 4 to 10 per cent of silica, 10 to 18 per cent of iron oxide, and 1.5 to 3 per cent of manganese oxide. All of these elements are plant food, but most soils contain an abundance of them. Duplex basic phosphate is essentially the same as Thomas phosphate or Thomas basic slag produced in Europe by the Bessemer basic process of steel manufacture. Thomas phosphate has been used for many years as a fertilizer in Europe and furnishes about one-half of the phosphoric acid consumed on the continent.

The manufacture of this fertilizer involves the solution of both agricultural and metallurgical problems. Standard basic pig iron contains less than 1 per cent silicon, from .20 to 1.50 per cent manganese, about .05 per cent sulphur and approximately .20 per cent phosphorus. Basic pig iron manufactured from Southern ores, however, contains from .85 to 1 per cent phosphorus.

In the usual specifications for open-hearth structural steel the phosphorus is limited to .06 per cent. Specifications covering structural steel for bridges, ships, fireboxes, boilers, etc., prescribe even lower limits, namely, .04 per cent. Southern mills roll large quantities of open-hearth rails in which the maximum permissible phosphorus is .04 per cent.

When manufacturing rails or other high-grade rolled-steel products from Southern pig iron contain-

ing .85 per cent phosphorus, it is necessary to remove over 95 per cent of the total amount of phosphorus existing in the pig metal, reducing it from .85 to .04 per cent. The carbon, in accordance with usual practice, is reduced to about .15 per cent. The blown metal is charged into a 100-ton primary open-hearth furnace of the tilting type. In the primary furnace, somewhat more than theoretical amounts of oxidizing materials, scale and iron ore, together with lime, etc., are added to oxidize the phosphorus, producing a tetra-calcium phosphate slag containing the equivalent of 18 to 22 per cent of phosphoric acid. The primary furnace heats are tapped into a ladle in the ordinary manner, the slag blowing over into slag boxes placed near the ladle. These boxes are of cast steel, with a capacity of about seven tons of slag. The steel may be poured directly into ingots if rolling specifications permit, but usually it is transferred to a second open-hearth furnace for further refinement in the ordinary manner.

The slag is transferred in the boxes previously mentioned to the fertilizer grinding plant, where it is dumped on the ground in the receiving shed. This shed is equipped with a 25-ton crane, provided with a magnet and skull cracker ball. The ball is used for breaking up the slag into chunks about eight inches in diameter. The broken pieces are picked up by a grab bucket and discharged into a steel receiving bin, from which they are delivered to the first series of crushers. The material is passed through three different types of crushing or grinding machines, which reduces it so that 80 per cent will pass through a 100-mesh screen.

The finely-ground product is elevated and delivered by screw conveyors into 1,000-ton concrete storage bins, of which eight are provided.

The bins are arranged to discharge their product onto screw conveyors, which deliver the material to a final set of elevators and screens. From the latter the finished material is discharged into a bagging machine. This machine packs the fertilizer in 100-pound bags, which are delivered direct to outgoing freight cars by means of a belt conveyor. Facilities also are provided for loading the material into the cars in bulk.

At considerable expense, a number of storage bins have been erected, with conveyors to and from them to facilitate a mixing arrangement which is necessary in order to produce a uniform product from the variable slags produced by the different heats in the steel plant, in order that the quality of the product as delivered may conform to the fertilizer laws of the different States.

According to figures given out August 1 by the Honolulu Stock Exchange there are continued indications that 1916 will be the banner year for Hawaiian sugar producers. Fifty-two Hawaiian plantations, the tabulations showed, paid a total of \$2,500,000 in dividends during July.

SODA PULP FROM ASPEN WOOD.*

By S. D. WELLS.†

The work of the Forest Products Laboratory in studying the influences of the various cooking conditions in the manufacture of soda pulp from aspen indicated that in varying any one of the four variables—steam pressure, initial concentration, amount of caustic soda used per unit of wood, or duration of cooking—and maintaining the other conditions constant, the amount of bleaching powder necessary to bleach the pulp to a standard white was constant for any given

relation of bleach consumption and yield to the amount of condensation during the cook, using the following conditions:

Concentration of NaOH, 90 grams per liter.

NaOH per 100-lb. chips, 25 lbs.

Maximum steam pressure, 120-lb. per sq. in.

Duration at maximum pressure, 4 hours.

Time necessary to reach maximum pressure, 1 hour.

The yield of pulp was increased from 43.5 per cent to 47.1 per cent of the weight of wood used, or an increase in the output of pulp from the same quantity of wood, using the same quantity of cooking chemicals and fuel of over 8 per cent, while the quality of the pulp was improved and the bleach consumption lowered from 13 to 11 lbs. of bleaching powder per 100 lbs. of pulp.

In seeking an explanation of this phenomenon, it is necessary to study the conditions in the digester during the cook. The consumption of caustic soda as shown in Fig. 3 was very rapid during the first hour

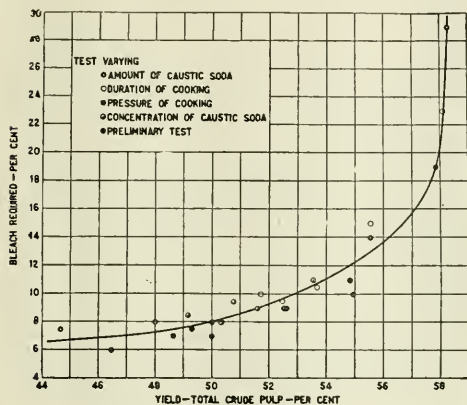


Fig. 1

yield of pulp. Twenty-four semicommercial cooks were made in studying these four variables, and the yields of pulp obtained plotted against the bleach consumption are shown in Fig. 1, obtained from Bulletin No. 80 of the United States Department of Agriculture.

This curve apparently indicates that any reduction in the consumption of bleach made by altering any of the four variables mentioned cannot be brought about without lowering the yield. All the cooks in the series were made, however, in a digester of only 70 gallons capacity and the condensation during the cook was about six times as great as in commercial sized apparatus of 3½ cords capacity. A series was, therefore, run where all the conditions were maintained constant, except condensation, and this factor was varied by using a combination of direct steam and indirect heating by means of a jacket in the lower portion of the digester.

The results obtained developed the remarkable fact that on increasing the amount of condensation the yields of pulp were increased and at the same time the quality of the pulp was slightly improved and the bleach consumption necessary to obtain a standard white was decreased. The curves in Fig. 2 show the

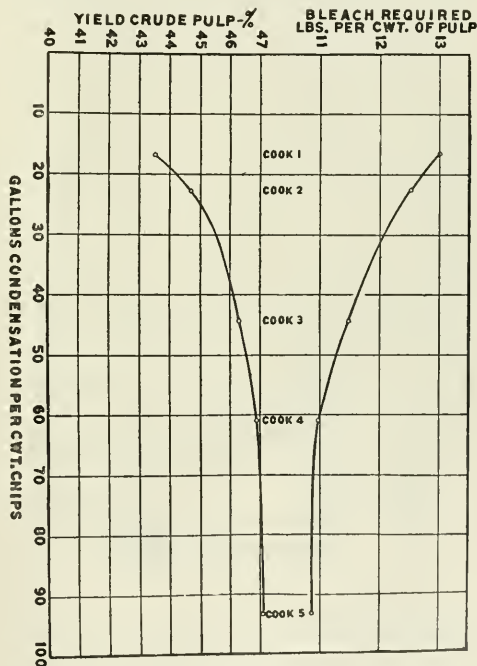


Fig. 2

and a half, but constantly decreased in rate and after the second hour had reached a point where only one-fifth of the original caustic was present as such.

The condensation of steam increased very rapidly during the first hour, due to the fact that the contents of the digester were being rapidly heated to the maximum temperature maintained during the succeeding four hours, and the shell and lagging must necessarily be brought to the same temperature. After the first

*Paper read before the 52d Meeting of the American Chemical Society at Urbana, Ill.

†Forest Products Laboratory, Madison, Wis.

hour the rate was greatly decreased, since only enough was needed to counteract the loss of heat through the shell and in steam vented to relieve gases and maintain circulation. The condensation for the five cooks of the series is shown graphically in Fig. 4.

During the four hours of maximum pressure, therefore, the concentration of caustic in the liquors was as follows:

	At end of first hour.	At end of fifth hour.
1	35 g. p. l.	8 g. p. l.
2	32 g. p. l.	7 g. p. l.
3	23 g. p. l.	5 g. p. l.
4	19 g. p. l.	4 g. p. l.
5	14 g. p. l.	3 g. p. l.

With the increased condensation, the pulp reduced from the outer portion of the chips was in all probability surrounded by much more dilute liquor and was therefore attacked less vigorously as a consequence of the very low adsorptive power of cellulose at those concentrations, as shown by the work of Leighton.¹

Aspen wood, on the other hand, has been found in our investigations to be capable of adsorbing at 100° C., as much as 20 per cent of its weight from

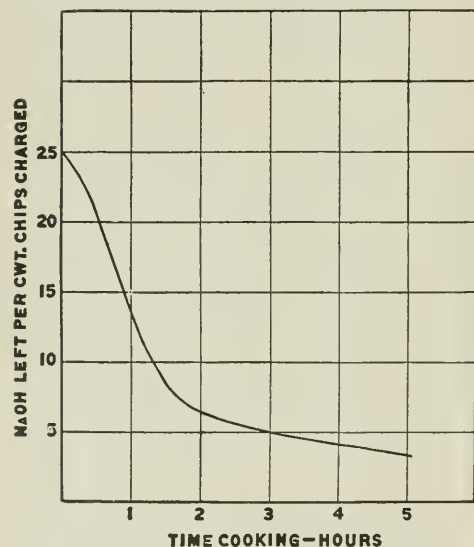


Fig. 3

solutions of 60 grams per liter and at the increased temperature the amount absorbed would be considerably greater. Our experiments with aspen chips have shown that during the first hour of the cook the caustic soda solution has penetrated the chips at nearly the original concentration. It is evident that the uncooked inner portions of the chips are capable of adsorbing sufficient caustic soda for their reduction but on the conversion of this material to pulp the adsorptive power is so reduced that the remaining caustic soda passes back to the liquor. The increased volume due

to condensation also more effectually removes the products of reduction from the wood and decreases the contamination of the pulp therefrom.

It is evident then that while the power of the caustic soda to reduce the ligno-cellulose is not diminished, the attack on the pulp is considerably decreased and the coloring of the pulp by the products of reduction

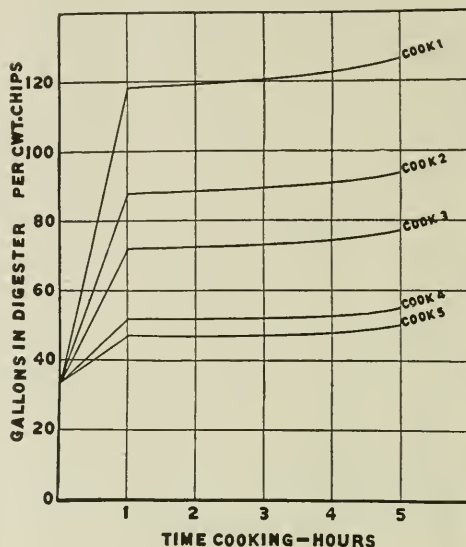


Fig. 4

is much less, thereby decreasing the bleach necessary to obtain a standard white. While no tests on a commercial scale have yet been tried it seems probable that the same advantages would be gained. The equivalent of the added condensation could be obtained by injecting hot water with the steam supplied, by which means perfect control would be comparatively simple. The only disadvantage would be the increased volume of the black liquor that would have to be handled in the recovery of the soda. With multiple effect evaporators, however, the excess water could be evaporated with very small increase in the fuel consumption and the increased production of pulp would be attained at extremely small cost.

The propaganda for the planting of the soya bean in Louisiana has made such progress that good sized crops will be put in. The Louisiana Cottonseed Crushers' Association representing some 30 cottonseed oil mills, has agreed to handle the soya bean as well. In North and South Carolina for several years cottonseed oil mills have been making use of the soya bean. It is stated they have been paying from \$1 to \$1.15 per bushel and have extracted on the average from one ton of beans 30 to 35 gal. of oil and 1,700 to 1,725 lbs. of meal.

¹The Absorption of Caustic Soda by Cellulose, Journal of Phy. Chem., Vol. XX, No. 1, pp. 32-50.

BENZOL PRODUCTION IN UNITED STATES IN 1915.

The recovery of the valuable by-products from American coke manufacture made big advances in 1915 and has now attained the proportions of an important industry. The value of these by-products last year was nearly \$30,000,000, a large increase over the previous high-water mark of \$17,500,000 in 1914. Although there were material increases in the output and value of gas, tar, and ammonia, which was to be expected with a greater output of by-product coke, the increase in benzol products was remarkable and presented the most interesting feature of the year in the coke industry. The value of these products rose from less than \$1,000,000 in 1914 to more than \$7,760,000 in 1915, according to C. E. Leshor, of the United States Geological Survey, Department of the Interior. Benzol has been recovered in this country from coke-oven gas for a number of years, but prior to 1915 the market was small and the prices low.

The awakening of the American people to the need for a dye industry and to a realization that such an industry can not spring full-grown from nothing but must be fostered and developed is now a well-known story. Few are aware, however, of the progress that has been made within a year in laying the foundations for future progress in that industry. Under the spur of almost fabulous prices for benzol products, retort coke-oven plants throughout the country quickly installed elaborate benzol-recovery systems and now save the valuable oils that not very long ago were being buried or wasted, or, if saved, were begging for a market.

In 1914 there were 14 benzol plants in the United States, but they were all controlled by one company, and therefore it is not feasible to publish the statistics of their production for that or previous years. Last year 16 additional coke plants were equipped with benzol apparatus, and the output was very greatly increased. The incentive for putting in this equipment was, of course, the opportunity to contract at war prices for benzol and other similar materials for use in making explosives for the European countries. When the demand from that source shall have ceased, the United States will be in possession of a large supply of the raw materials from which dyes and chemicals are made and will be able, if trade conditions are right, to enter into the manufacture of these essential materials on an ever-increasing scale. The prompt and successful manner in which, in 1915, under favorable conditions, the producers increased the benzol supply and entered the field of dye manufacturing on a larger scale than ever before demonstrates the fact that in this country technical ability and business courage are not lacking and promises well for the future progress of the industry.

The benzol products obtained in 1915 amounted to 16,600,657 gallons. More than 13,000,000 gallons of

the total output was reported as crude light oil and had an average value of 33 cents. Some of the plants have their own stills and refineries, and the pure benzol reported from those sources amounted to 2,516,483 gallons, with an average value of nearly 57 cents, at least three times the value of crude benzol before the war, and 623,506 gallons of toluol, with an average value of \$2.45 a gallon. Crude benzol, which in 1914 was used to some extent for motor fuel, contained the toluol, which is now separated out and sold at fancy prices.

More than 138,000,000 gallons of tar was obtained from coke ovens and sold for \$3,568,384 in 1915.

The ammonia, of which nearly 100,000 tons was reported as sulphate and the remainder as liquor (10,626,612 gallons) and anhydrous ammonia (30,002,196 pounds), brought a total of \$9,867,475 to the producers. Surplus gas to the extent of 84,356,000,000 cubic feet, valued at \$8,625,000, was sold or used. Of that quantity 17,196,000,000 feet was used as illuminating gas, 27,591,000,000 feet as domestic fuel, and 39,569,000,000 feet as fuel for steam raising, open-hearth furnaces, gas engines, and other industrial purposes. These by-products, which had a total value of \$29,824,579, were obtained by the carbonization of 19,500,000 tons of coal, from which was also obtained 14,000,000 tons of coke, valued at \$48,558,325. The total value of the coke and by-products was more than \$78,382,904.

TABLE I.—BY-PRODUCTS OBTAINED FROM COKE-OVEN OPERATIONS
IN 1915.

Product.	Quantity.	Value.	Average value.
Tar obtained and sold, gallons.	138,414,601	\$3,568,384	\$0.026
Ammonia obtained and sold:			
Sulphate, pounds	199,900,487	5,648,958	.028
Liquor, gallons	10,626,612	1,240,473	.117
Anhydrous, pounds	30,002,196	2,978,044	.099
Gas produced, M cubic feet	213,667,614		
Surplus gas sold or used:			
Illuminating, M cubic feet	17,196,426	3,083,311	.179
Domestic fuel, M cubic feet	27,590,624	3,158,129	.114
Industrial fuel, M cubic feet	39,568,864	2,383,450	.060
Benzol products:			
Crude light oils, gallons	13,082,678	4,304,281	.33
Secondary light oils, gallons	182,039	28,731	.16
Benzol, gallons	2,516,483	1,428,323	.568
Toluol, gallons	623,506	1,529,803	2.45
Solvent naphtha, gallons	196,151	46,233	.24
Naphthaline, pounds	465,865	46,959	.10
Other products*		379,491	...
		\$29,824,579	
Coke, short tons	14,072,895	48,558,325	\$3.45
		\$78,382,904	

*Includes breeze, retort carbon, domestic coke and coke dust, and aniline oil.

Chemical plants in McKean, Elk, Forest and Warren Counties, Pennsylvania, for the first time in many years will operate at full capacity throughout this summer. In other years a majority of these plants operated on a small scale during the summer, while others closed down entirely. The demand for acetate of lime is the principal cause of this activity.

STUDIES ON THE EXTRACTION OF ROSIN FROM WOOD. I—EXPERIMENTS USING A PETROLEUM SOLVENT.*

By R. C. PALMER¹ and H. R. BOEHMER.²

PURPOSE OF WORK.

From a technical viewpoint, the process of extracting rosin from wood with chemicals offers a promising possibility for the utilization of "fat" stumps and other waste resinous wood. In the simple steam distillation process only the volatile constituents of the wood are recovered and this method is no longer industrially feasible on this account. In the destructive distillation process, the products are charcoal, tar, and a turpentine more or less contaminated with products from the destructive distillation of the rosin and wood substance. This turpentine, at best, does not bring as high a market price as steam-distilled wood turpentine, although the recent introduction of temperature-controlled processes has removed this objection to a large extent. Compared with these two processes, the so-called solvent or extraction process affords the recovery of wood turpentine and pine oil comparable in quality and value with the oils from steam distillation and also a medium grade rosin whose market value, under normal conditions, is practically equal to the combined value of charcoal and tar from the destructive distillation process. However, the market value is less likely to fluctuate for tar and charcoal than for rosin. Strictly speaking, the extraction and distillation processes are not comparable, because the products are quite different. These processes represent the two types which taken together cover most of the possible products to be obtained from resinous wood.

Of the several different processes proposed for treating wood, the destructive distillation method, which is by far the oldest, is also at the present time apparently the best established from the standpoint of profitable commercial operation.³ The principal difficulties that have been encountered in the extraction process have been: (1) an unstable market price for rosin, and (2) high cost of operation, due largely to an excessive loss of solvent. In attempting a solution of these difficulties, there are then at least two lines of attack which may give this process a better opportunity for commercial success: (1) obtaining another product which would not be subject to very great market variations, and (2) decreasing the operating cost. The use of the extracted wood as a raw material for paper pulp has been suggested several times as a possible solution of the problem of obtaining another product. Extraction by the usual method requires wood so finely divided (shredded wood) to yield a high proportion of the rosin that the

extracted material is not suitable for pulp. If the wood is large enough for pulp, the yield of rosin is decreased. Considering the high operating costs as due largely to the loss of solvent, it would seem that the problem here is largely mechanical, and its solution should not offer very great difficulties.

With these ideas in mind, it was felt that a careful study should be made of some of the fundamental operating variables of the process.

The experiments were carried on at the Forest Products Laboratory, Madison, Wisconsin. The material consisted of longleaf pine stumps from Louisiana, donated by the Long-Bell Lumber Company of Kansas

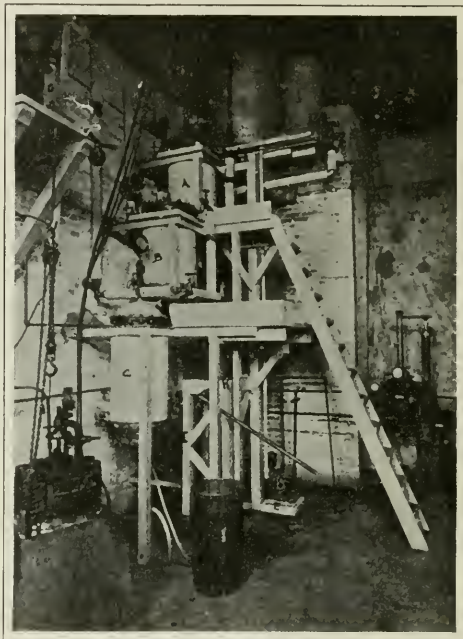


Fig. 1

City, Missouri. Acknowledgment is made to Mr. S. D. Wells, Engineer in Forest Products, of the section of pulp and paper, for making the experiments on the suitability of extracted chips for pulp.

DESCRIPTION OF PROCESS.

About fifteen patents have been granted in the United States for extraction processes and apparatus since 1909, and one or two plants were built and had been operated before that time. The different patents vary chiefly in the treatment of the wood before and after applying the solvent, in the manner of applying the solvent, and in the solvent itself. In general, the process, as carried out in the commercial plant, consists in first steaming the finely divided wood to recover the volatile constituents (turpentine and pine oil), followed in some cases by evaporating out of the wood as much of the condensed steam as possible. The

*From Journal of Industrial and Engineering Chemistry.

¹Chemist in Forest Products. Forest Products Laboratory, Madison, Wis.

²The data obtained in these experiments were submitted by this author in partial fulfillment of the requirements for the degree of B.S. in Ch.E. in the University of Wisconsin.

³Journal of Industrial and Engineering Chemistry, 6 (1914), 151.

solvent is then applied to the wood to dissolve out the rosin. After extraction, the wood is treated to recover the solvent adhering to, or absorbed by the chips. Evaporation of the solvent leaves the rosin as a residue, the solvent being recovered for subsequent extractions.

EXPERIMENTAL.

Apparatus.—The apparatus used in the experiments was an extraction battery composed of three retorts, *A*, *B*, and *C*, shown in Fig. 1. The chips were placed in the perforated baskets, *D*, each retort holding from 30 to 35 lbs. of wood. The battery was so arranged that the solvent could be forced by means of a pump, *E*, to a storage tank, *F*, from which it flowed by gravity into any one of the retorts and from that retort to each one below it. Each unit was independent of the others so that different operations could be carried on at the same time. Each retort was also connected to a vacuum pump, *G*, through a condenser, *H*, and receiver, *I*, and equipped with an open coil for direct steam and closed coils for heating the solvent.

As it was desired to boil the solvent in contact with the chips the apparatus was so arranged that this could be done without decreasing the solvent by evaporation. This was accomplished by connecting the vapor outlet line of each unit to a condenser, *J*, and receiver or trap, *K*, placed above the battery. The trap was connected to the bottom of each retort and thus allowed the vaporized solvent, after it was condensed, to flow continuously back into the retort as in a reflux condensing apparatus. By connecting the top of each retort to the top of the trap, the vapor conditions were equalized and the solvent was prevented from backing up. With these "equalizers" open, the solvent in any retort could be boiled under pressure for any desired length of time with a constant reflux of the condensed vapors.

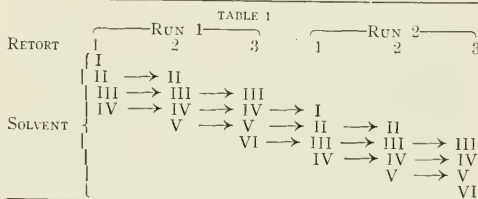
The simple still, *L*, was used for the evaporation of the saturated solvent to recover the rosin. The still was equipped with a steam jet and was connected through the receiver, *M*, to the vacuum pump to facilitate the removal of water and heavy oils from the rosin.

Solvent.—Since a petroleum distillate has been most frequently used commercially as a solvent there was selected for the experimental work, a special gasoline furnished on a guarantee to boil between 70 and 150° C. It was found, however, that the material contained at least 20 per cent boiling under 70°, a portion boiling as low as 30°. The solvent was, therefore, fractionated in a laboratory column (4 in. in diameter), the fraction below 70° C. being removed. By distillation in a Hempel column the solvent used gave 4 per cent boiling below 70° and 95 per cent boiling below 150°.

Extraction.—It was desired to make the laboratory study as comparable as possible with extraction in a continuous commercial extraction battery. In an ex-

traction system of this type, all units receive exactly the same treatment and in no case is fresh solvent run on to fresh material, but the solvent most nearly saturated with the substance being extracted is run on to fresh material and the most nearly spent material receives a final treatment with fresh solvent. This condition was approximated in a laboratory test, providing a system of four washes for each unit by employing six solvents. Three of these were distilled at the end of each run and three were used for the next run without recovering the rosin. The method may be better explained diagrammatically by referring to Table I.

Solvents I, II and III in each run were distilled for the recovery of rosin, having extracted the rosin from the wood in four retorts, while Solvents IV, V



and VI become Solvents I, II and III, respectively, for the next run. Solvent I, in Retort 1; II, in Retort 2; and III, in Retort 3, represent the action of nearly saturated (theoretically) solvents on wood which has not been previously extracted. Solvent IV, in Retort 1; V, in Retort 2; and VI, in Retort 3, represent the final extraction of nearly spent chips with fresh solvent. Before beginning the first run, a preliminary run was necessary in order to secure Solvents I, II and III, for the first test. After the retorts were charged in these tests, they were not opened until the dried extracted chips were removed.

The procedure used in conducting any test was briefly as follows: The chips were first steamed under 30 lbs. pressure⁶ until no more turpentine and pine oil were obtained; the retorts were then connected to the vacuum pump from 30 to 60 min. to remove as much of the moisture as possible, steam being kept in the closed coils to facilitate evaporation. The solvent was then introduced until the chips were just covered and was then brought to boiling by means of the steam in the closed coils. The reflux system was open so that the vaporized solvent would condense, and flow back into the retort. In case the extraction was conducted under pressure the valves connecting the retort to the reflux were closed until the desired pressure in the retort was reached. The line connecting the retort with the reflux was then opened and the pressure controlled by the amount of steam passed into

⁶In purchasing solvents of this type commercially, the importance of contracts calling for extremely rigid specifications is indicated by this experience. With such a large proportion of a very low boiling fraction in the solvent it would be impossible to prevent a high solvent loss.

⁷Journal of Industrial and Engineering Chemistry, 4 (1912), 789; also F. S. Bull. 109, "Distillation of Resinous Wood With Saturated Steam."

the closed coils. After extraction the solvent was transferred to the next retort, or in case it was the last extraction for that solvent, it was passed through a condenser which delivered it cold to the container. When the extraction was made under pressure it was better to relieve the pressure before drawing out the solvent; this was readily done by turning off the steam and allowing condensation to continue in the reflux. When the solvent was drained out after the last extraction, that remaining in the chips was removed by steaming first at atmospheric pressure until no more solvent came off, and finally at 30 lbs. pressure for a few minutes. To insure that all the solvent was removed, the retort was then connected to the vacuum pump for about one hour. In only a few cases, however, was any more solvent recovered in this last step.

As soon as each solvent was removed after final extraction it was thoroughly stirred, and a sample taken. The weight of each solvent was taken before it was used in any run and after its final use in that run. The intermediate weights when a solvent passed from one retort to the next were not taken. In other words, the total amount of wood in the three units of the battery was considered as the charge for the run rather than that in each retort as a separate unit. Since only three solvents were redistilled in any run and these contained some rosin from a previous run, it was not possible to determine the rosin yield from the actual rosin recovered by the redistillation of the solvent. The yields were determined by an analysis of the solvents. The total yields from several runs checked very well with the analyses.

ANALYSES.

The efficiency of any extraction was based on a comparison of the amount of rosin in the solvents, as determined by analysis, and the amount of rosin contained in the charge, as determined by an analysis of an average sample of the wood.

Wood.—A sample of the charge was taken by quartering the wood in each retort until the desired amount (about $\frac{1}{2}$ lb.) was obtained. A portion of the sample from each retort was then ground to the fineness of sawdust and a moisture determination made by the xylol method,⁶ generally employed in estimating moisture in wood which contains a volatile oil. An equal portion of the finely ground sample from each retort was extracted in a Soxhlet with chloroform. On drying the extracted sample to constant weight at 110° C. the weight of the wood free from moisture, rosin, and volatile oil was obtained. The extract from the Soxhlet was then evaporated in an oil bath kept at 150° C. After the chloroform had all distilled off a small jet of steam at slightly reduced pressure was passed through the rosin. This was continued for $\frac{1}{2}$ hr. and the residue was then dried by using a much higher vacuum for $\frac{1}{2}$ hr. intervals, without the steam, until the rosin showed a loss of less than 0.2 per cent for two successive treatments. Continued heating

caused some decomposition, so that drying could not be carried to constant weight. The final residue was then taken as rosin. Since moisture and rosin and the extracted wood were determined the volatile oil was estimated by difference. The method is not entirely satisfactory, but since it is not practicable to determine volatile oil in so small a sample, and thus determine rosin by difference, it was felt that rosin could be determined as the non-volatile chloroform extract. Duplicates checked within 0.003 to 0.005 per cent and errors that were large enough to be of consequence to the experiment fell back on the sample itself. It is, furthermore, not strictly correct to compare the petroleum extraction with the chloroform control since there were probably small portions of the rosin that were insoluble in petroleum but were soluble in chloroform.⁷ The extraction efficiencies were, therefore, lower than if based on the total petroleum soluble rosin present in the wood.

Extraction.—The yield of rosin in the tests was determined, as stated above, by an analysis of the different extracts. The amount of rosin in a weighed portion (about 200 g.) was determined in practically the same manner described for estimating the rosin in the chloroform extract, except that the residue was not steam-distilled because no appreciable amount of high boiling oils, such as pine oil, was left in the wood and rosin after the chips were thoroughly steamed.

SCOPE OF EXPERIMENTS.

The experiments in this first series included a study of the more important fundamental operating variables on the efficiency of the extraction: (1) time, (2) pressure, (3) size of material, (4) moisture, and (5) effect of rosin content on the percentage yield of rosin, based on the amount originally present. The tests also included a preliminary study of the suitability of the extracted material for paper pulp. Two

⁷Allen, "Commercial Organic Analysis," chapter on Colophony.

TABLE II—EFFECT OF VARIOUS FACTORS ON EXTRACTION OF ROSIN

Effect Illustrated	Run No.	Time Min.	Chip In.	Pressure Lbs.	% Rosin in Wood	Rosin Yield Per ct.
Time	1	15	3/16	0	29.92	72.6
	2	45	3/16	0	25.10	75.0
	3	15	3/16	30	23.60	91.60
	4	45	3/16	30	25.92	93.70
	11	15	5/8	30	12.96	68.5
	12	45	5/8	30	12.23	68.9
Pressure	1	15	3/16	0	29.92	72.6
	6	15	3/16	30	27.43	94.3
	5	15	3/16	55	29.35	85.3
	2	45	3/16	0	25.1	75.0
Size of Chip.....	4	45	3/16	30	25.92	93.7
	12	45	5/8	30	12.5	68.9
	9	15	3/16	30	10.73	88.8
	11	15	5/8	30	12.9	68.5
Moisture, High.... Low.....	4	45	3/16	30	25.92	93.7
	12	45	5/8	30	12.5	68.9
	9	15	3/16	30	10.73	88.2
	10	15	3/16	30	10.7	72.1
Rosin Content	7	15	3/16	0	13.32	70.8
	1	15	3/16	0	29.92	73.6
	9	15	3/16	30	10.73	88.8
	3	15	3/16	30	23.60	91.6
	6	15	3/16	30	27.43	94.8

⁶F. S. Circ. 184, "Estimation of Moisture in Creosoted Wood."

sizes of chips, averaging 3/16 in. and 5/8 in. with the grain of the wood, were selected for the tests. The 3/16-in. chip is larger than the usual commercial chip used in the extraction process, but is considered the minimum size for making pulp. The material was prepared in a semi-commercial pulp chipper. The wood in each case comprised the whole of the stump including the outer bark. All of the stumps had the roots removed and were practically free from earth and sand.

RESULTS.

Effect of Time.—Fig. 2 based on the results of Runs 1 and 2 (Table II) shows the progress of the extraction. The curve is obtained by plotting the percentages of rosin recovered as ordinates, and the time the solvent was in contact with the wood as abscissas. Referring to Table I, which shows the pro-

sponding curves for Runs 3 and 4 and 11 and 12, but no logical explanation of this was made evident during the experiment.

Effect of Pressure.—The progress of the extraction for Runs 1, 5 and 6, shown in Fig. 3, is typical of the effect of pressure. The figure shows that the rosin recovered was increased from 72.6 per cent to 94.3 per cent by increasing the pressure from 0 to 30 lbs. At 55 lbs. pressure there is an apparent break in the curve, and a decided decrease in per cent recovery as compared with 330 lbs. pressure. Since, in a study of the penetrance of creosote in longleaf pine heartwood at the Forest Products Laboratory,⁸ a decided decrease was noted as the pressure was increased from 50 to 75 lbs., the cause of the decreased efficiency of extraction may be a physical one. It seems more probable, however, that the explanation

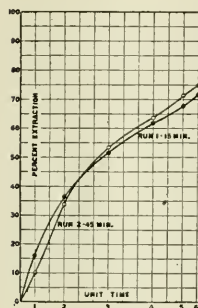


Fig. 2—Effect of Time. Chip, 3/16 In. Pressure, 0 Lbs. Min.

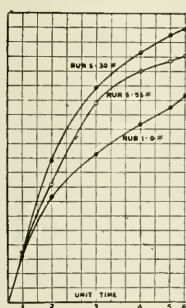


Fig. 3—Effect of Pressure. Chip, 3/16 In. Extraction, 15 Min.

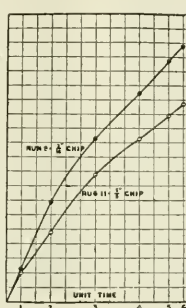


Fig. 4—Effect of Size of Chip. Pressure, 30 Lbs. Extraction, 15 Min.

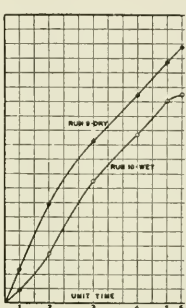


Fig. 5—Effect of Moisture. Chip, 3/16 In. Pressure, 30 Lbs. Extraction, 15 Min.

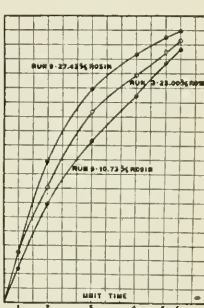


Fig. 6—Effect of Rosin Content. Chip, 3/16 In. Pressure, 30 Lbs. Extraction, 15 Min.

cedure used in the test, it is seen that in any run Solvent I is in contact with the wood only for the unit time, which is 15 min. for Run 1. Solvent II, however, is in contact with the wood twice as long as Solvent I, Solvents III and IV three times as long as Solvent I, and Solvents V and VI for the same time as Solvents II and I, respectively. The units on the abscissa, therefore, represents the progress of extraction. Since each solvent was analyzed before its first and after its last application, the proportion of the total rosin extracted by each solvent in any run could be determined.

It will be seen that the effect of increasing the time from 15 to 45 min. is slight for the three sets of conditions used, and for practical purposes 15 min. is evidently the maximum time necessary. In Runs 3 and 4, which gave the highest yields, the efficiency was increased only 2.1 per cent when the time was increased threefold. In Fig. 2 it will be noticed that in the 15-min. extraction a larger proportion was recovered with the first two solvents than when the time was 45 min. This same condition was shown in corre-

sponding curves for Runs 3 and 4 and 11 and 12, but no logical explanation of this was made evident during the experiment.

Effect of Size of Chip.—Fig. 4 shows the curve of extraction for Runs 9 and 11. Increasing the size of the chip to 5/8 in. decreases the efficiency of extraction from approximately 90 to about 70 per cent, and the result is practically independent of the time of extraction. In the studies of the penetrance of creosote in longleaf pine heartwood referred to above, it was also shown that the ratio of longitudinal to radial penetration was 26:1, and of longitudinal to tangential was 100:1. For practical purposes the action of the solvent is, therefore, almost entirely in the longitudinal direction, which is also the same direction as most of the resin ducts, that is, with the grain in the wood.

⁸U. S. Dept. of Agric. Bull. 101, "Relative Resistance of Various Conifers to Injection With Creosote."

The decrease in the rosin removed from the longer chips is then undoubtedly a question of decreased penetration of the solvent into longer resin ducts. Since giving the solvent a longer time to penetrate does not increase the yield, as seen in Runs 11 and 12,⁹ it seems safe to predict that additional pressure is necessary to penetrate to the center of the longer chips. A continuation of those studies will determine the accuracy of this supposition.

Effect of Moisture.—After steaming the chips for the removal of volatile oil preparatory to extraction, it was the usual procedure to pull a vacuum of about 20 in. on the retort for $\frac{1}{2}$ hr., the retort being kept hot by means of steam in the closed coils in order to remove as much as possible of the excess moisture caused by steaming. In general, the water removed in this way was equivalent to about 30 per cent of the dry weight of the wood, but the ratio of this amount to the total moisture in the chips after steaming was not determined. As several patents call attention to this feature of the process it was desired to determine its effect. A run was made, therefore, in which the vacuum was omitted and the solvent was run directly to the chips after steaming. The results of this run compared to a similar run in which the vacuum was used are given in Table II and the progress of the extraction for the two runs is shown in Fig. 5.

The effect of removing a comparatively small amount of moisture by the vacuum treatment is more pronounced than might be supposed, since the efficiency is increased over 15 per cent. It will be noted in the curve that the extraction is more retarded at the start; and it is, therefore, quite possible that the excess of moisture is removed by the first wash, after which the extraction proceeds more normally. When the water has once boiled off with the gasoline vapor and, on condensing in the reflux, flows back into the bottom of the retort, it probably does not interfere to any extent with the extraction. By taking the condensed solvent from the top of the trap in the reflux line it would be possible to get rid of this excess water in a short time, since the moisture could be drawn off at the bottom of the trap and thus be removed from the system. With such an arrangement, increasing the time of extraction should then give almost as high efficiency as when the chips are dried by the vacuum unless, in addition to removing the surface moisture, the vacuum has some mechanical action of opening up the ends of the exposed resin ducts and thus facilitates the penetration of the solvent. It is desired to test this point in future experiments.

Effect of Rosin Content.—These tests on the effect of different variables were made on samples of quite different rosin content, one lot being comparatively rich and varying from 23 to 30 per cent rosin, and

another lot being comparatively low in rosin and varying from 10½ to 13½ per cent. An analysis of the data (Table II) from runs made under the same extraction conditions but with chips of different rosin content is of interest.

Runs 3, 6 and 9, made at 30 lbs. pressure and 15 min. extraction, are shown graphically in Fig. 6. It is seen from the table that a higher percentage of rosin is recovered from woods of greater rosin content and the higher recovery is evident throughout the progress of the extraction as shown in the figure. This is probably due to the fact that there is a larger proportion of the rosin which has saturated the cells surrounding the resin ducts proper in the richer wood and this rosin is, therefore, made more accessible to the action of the solvent. The wood containing 13.5 per cent rosin is about as low in rosin as could be extracted commercially.

SOLVENT LOSS.

The apparatus used in the test was not found to be entirely suitable for the study of the loss of solvent. Because of errors in construction the solvent collected in pockets in the piping and it was, therefore, not recovered until another run. There were also noticeable leaks at several points. In general it was apparent that extraction under pressure tended to increase slightly the amount of solvent retained in the chips but there was no difficulty in recovering this solvent on subsequent steaming. With evident leaks in the apparatus, increasing either time or pressure would,

TABLE III—SOLVENT LOSSES IN VARIOUS RUNS

Run No.	Chip In.	Pressure Lbs.	Time Min.	Solvent Loss	
				Per cent.	Rosin Yield Per cent.
1.....	3/16	0	15	2.38	72.6
2.....	3/16	0	45	6.87	75.0
3, 6, 9 (Av.).....	3/16	30	15	3.46(a)	91.5
4.....	3/16	30	45	4.30	93.7
5.....	3/16	55	15	3.74	85.3
11.....	5/8	30	15	3.46	68.5
12.....	5/8	30	45	3.85	68.9

(a) Varied from 3.16 to 3.79.

of course, increase the solvent loss. The amount lost in several of the runs is shown in Table III. While the data do not show clearly the effect of the different time and pressure conditions on solvent loss, it may be noted that a longer time seemed to give a greater increase in solvent loss than a higher pressure.

It was possible to determine approximately the proportion of this loss that occurred in the redistillation of the solvent and this averaged about 10 per cent of the total. The solvent loss will be taken up in detail in a later study.

FORMATION OF A PRECIPITATE.

An interesting point that came up in the experiments was the discovery of a precipitate in the solvent removed from the chips, especially after extracting wood of high rosin content. Yaryan¹⁰ calls attention to a black pitchy substance which precipitates out of the rosin solution and which he says is due to the action of fire on the stumps or lightwood. The precipitate was at first dark brown, later becoming

⁹The more pronounced effect of increasing the time used in Run 4 to that used in Run 9 may be largely explained by the higher rosin content of the wood used in Run 4, as will be shown in the discussion to follow.

¹⁰U. S. patent 934,257.

black; it was quite sticky, and was first thought to be some constituent of the rosin insoluble in petroleum. Further examination indicated that it was largely basic ferric acetate which carried down a small amount of rosin with it. It was no doubt formed by the attack of the iron retorts by the free acetic acid occurring in the old wood, the acetate of iron formed becoming the insoluble basic salt at the high temperature of the boiling solvent. In some of the runs the precipitate amounted to as much as 1 per cent of the dry weight of the wood.

SUITABILITY OF THE EXTRACTED CHIPS FOR PULP.

Only preliminary experiments have been made with the extracted chips. It was desired first to determine the quality of pulp that could be obtained from the 3-16-in. chip although it seemed that this size would give too short a fiber length for good pulp. By using the sulphate process the unscreened chips from Runs 6 and 9 were cooked in a semi-commercial digester. The time of cooking was 1 hour in getting up the pressure, and 2 hours at 100 lbs. pressure. The cooking liquor contained 15.7 lbs. NaOH and 7.5 lbs. Na_2S per 100 lbs. of wood. The pulp yield was 43.2 per cent of the dry chips. Two beater treatments were made on the "half stuff," the duration of beating being 5 hours in each case. In one run the beater roll was hard down during the last hour, while in the second run the stock was much more dilute and the roll was set so as to give a comparatively light brush. The pulp was run over the machine and the sheets from the two beater treatments gave the following strength tests. The figures from what may be considered a No. 1 Kraft are given in the following table for comparison.

Paper.	Strength Points per lb. in	Schopper Test Breaking Length Test in Meters.	Folding Times.	Weight per Ream Lbs.
Beater Run No. 1.....	0.72	5425	800	40
Beater Run No. 2.....	0.65	4730	367	38
No. 1 Kraft.....	1.00	6000	1500	40

While Run 1 was stronger, Run 2 gave a softer sheet. Both were a very fair grade of No. 2 Kraft. Further tests will be made by using the larger chips, but since the small chip gives such promise of being suitable for pulp, they are more desirable, since it is possible to get so much higher yields of rosin from them by extraction.

CONCLUSIONS AND THEIR COMMERCIAL APPLICATION.

The results of these experiments seem to indicate that a solution of the problem of obtaining another product in the extraction of resinous wood by the solvent process may be found in using a larger chip, whose minimum size is 3-16 inch, and extracting under a maximum pressure of 30 lbs. by using four washes of 15 min. each. A closed type of battery in which the vaporized solvent can be returned continuously to the retort is advantageous for extracting under pressure. Extraction under pressure for a short time is shown to give much higher yields of rosin than no pressure for a longer time.

As noted in the results given above, the yields by

petroleum extraction are based on control analyses made by using chloroform as solvent. It was observed that certain constituents of the rosin are insoluble in petroleum but are soluble in chloroform. Since it is also shown that increasing the time of extraction has no appreciable effect at 30 lbs. pressure, and since 94.8 per cent were recovered under those conditions, it would seem possible that practically all of the petroleum-soluble rosin was extracted at this pressure. It is probable, therefore, that a lower pressure would be as efficient as 30 lbs.

Chips as small as 3-16 in. are apparently suitable for paper pulp as they gave a good grade of No. 2 Kraft by the sulphate process. Chips of this size could probably be most advantageously cooked commercially in a rotary type of digester. A plant extracting wood yielding about 250 lbs. or 1.09 bbls. of "F" grade rosin per ton (89 per cent yield of 14.0 per cent rosin), which is about the minimum for practicable commercial operation, would produce extracted chips suitable for making about 750 lbs. of pulp per ton of wood. A 50-ton extraction plant would then supply a 20-ton pulp mill, or since an extraction plant might require about three-quarters of its extracted chips as fuel in case it were not advantageous to buy other fuel, a 200-ton plant would have chips for fuel and still could supply a commercial pulp mill of practicable size.

It is difficult to give cost figures to cover the variety of contingencies met with commercially, but the following estimates of average practice show clearly the effect on the net returns of obtaining extracted chips as an additional valuable by-product.

COST ESTIMATE PER TON ON 200-TON EXTRACTION PLANT.

Cost of Operation.	6 gals. turpentine and
Prices for past 15 years.	pine oil at 40c.....\$2.40
Returns at Average.	250 lbs. rosin at 15c
Wood.....\$2.25	(3.77½ per net bbl. of
Solvent: 7½ gals. at 12c. .90	230 lbs.).....3.75
Fuel: ¾ ton extracted	
chips at no cost......00	
Cooperage......65	Cost of operation.....5.92
Superintendence and labor	
.....87	Net profit.....\$0.23
Selling and shipping, including freight......72	Selling price 250 lbs. extracted chips at \$1.00
Taxes, insurance and depreciation over 15 yrs. .35	per ton......25
Repairs and miscellaneous......18	Net profit with chips as by-product.....\$0.48
	\$5.92

The plant would pay 5.5 per cent on an investment of \$250,000 without the chips and 11.5 per cent assuming the chips to be worth \$1.00 per ton for pulp, which is a low estimate since the material would be in condition for immediate pulping.

Exports of ferro-carbon-titanium to England alone, as given by the Titanium Alloy Mfg. Co., are as follows: 1914, 170,240 lbs.; 1915, 471,500 lbs.; 1916 to June 1, 594,756 lbs. In addition, considerable shipments have been made to Japan. The demand is reported large, but expansion of production is dependent on the question of power.

INDUSTRIAL RESEARCH AND ITS FRUITAGE.*

By ARTHUR D. LITTLE.

Cornell has been especially alive to the scientific needs of industrial practice, and a long experience with technical assistants enables me to say that I have found none better equipped to cope with the miscellaneous problems of industrial research than the graduates of Cornell. It may, in fact, be stated generally that the quality of advanced chemical training now afforded in this country is on a par with the best obtainable in Germany, and that home-trained American youth adapt themselves far more efficiently to the requirements and conditions of our industries than do all but the most exceptional German doctors of philosophy who find employment here.

Several of the great universities of the Middle West, notably Wisconsin and Illinois, have placed themselves closely in touch with the industrial and other needs of the community and are exerting a fundamental and growing influence upon affairs. In the East Columbia has recently established a particularly well-equipped laboratory for industrial chemistry and is broadening its work in this department.

The Universities of Kansas and of Pittsburgh are carrying forward an especially interesting experiment in the operation of industrial research fellowships, supported by the special interests directly concerned. These fellowships endow workers for the attack of such diverse subjects as the chemistry of laundering, the chemistry of bread and baking, that of lime, cement and vegetable ivory, the extractive principles from the ductless glands of whales, the abatement of smoke nuisances, the technology of glass and many others. The results obtained are intended primarily for the benefit of the supporters of the individual fellowships, but may be published after three years. The holder of the fellowship receives a proportion of the financial benefits resulting from the research, and the scale of sums allotted has progressively risen from \$500 a year to \$2,500, and even to \$5,000. While some doubt may reasonably be expressed as to the possibility of close individual supervision of so many widely varying projects, the results obtained thus far seem entirely satisfactory to those behind the movement, which has further served to emphasize strongly the willingness of our manufacturers to subsidize research.

The present vitality and rate of progress in American industrial research is strikingly illustrated by its very recent development in special industries. It has been said that our best research is carried on in those laboratories which have one client, and that one themselves.

Twenty-five years ago the number of industrial concerns employing even a single chemist was very small,

and even he was usually engaged almost wholly upon routine work. Many concerns engaged in business of a distinctly chemical nature had no chemist at all, and such a thing as industrial research in any proper sense hardly came within the field of vision of our manufacturers. Many of them have not yet emerged from the penumbra of that eclipse, and our industrial foremen as a class are still within the deeper shadow. Meantime, however, research has firmly established itself among the foundation stones of our industrial system, and the question is no longer what will become of the chemists. It is now what will become of the manufacturers without them.

In the United States today the microscope is in daily use in the examination of metals and alloys in more than 200 laboratories of large industrial concerns. And indeterminate but very great amount of segregated research is constantly carried forward in small laboratories, which are either an element in some industrial organization or under individual control. An excellent example of the quality of work to be credited to the former is found in the development of cellulose acetate by Mork in the laboratory of the Chemical Products Company, while a classic instance of what may be accomplished by an aggressive individualism plus genius in research is familiar to most people through the myriad and protean applications of Bakelite. The rapidity of the reduction to practice of Baekeland's research results is the more amazing when one considers that the distances to be traveled between the laboratory and the plant are often, in case of new processes and products, of almost astronomical dimensions.

There are the highly organized, munificently equipped and splendidly manned laboratories of the du Pont Company, the General Electric Company and the Eastman Kodak Company. There are in the country at least 50 other notable laboratories engaged in industrial research in special industries.

The expenditure of several of them is more than \$300,000 each year.

The United States Steel Corporation has not hesitated to spend that amount upon a single research, and the expenses of a dozen or more laboratories probably exceed \$100,000 annually.

One of the finest iron research laboratories in the world is that of the American Rolling Mills Company. Equally deserving of mention from one aspect or another are the laboratories of the Fire Underwriters, the National Carbon Company, the Solvay Process Company, the General Bakelite Company, Parke, Davis & Co., the Berlin Mills Company, the United Gas Improvement Company, the National Electric Lamp Association, Swift & Co., the Pennsylvania Railroad and many others.

Research in the textile industries has been greatly stimulated by the various textile schools throughout the country, of which the Lowell Textile School with its superb equipment is perhaps best known. The

*A letter published in the Public Ledger, Philadelphia, Pa.

fermentation industries have been brought upon a scientific basis largely through the efforts of the Wahl-Henius Institute at Chicago and other special schools. In the paper industry general research is mainly confined to the Forest Products Laboratory at Madison, its branch laboratory for wood pulp at Wausau, the Bureau of Standards, the Paper and Leather Laboratory of the Agricultural Department and the laboratory of Arthur D. Little, Inc., at Boston. Our own special equipment for this purpose includes, as does that of some of the other laboratories named, a complete model paper mill of semi-commercial size.

There is no school of paper making in the country, and one of our most urgent industrial needs is the establishment of special schools in this and other industries for the adequate training of foremen who shall possess a sufficient knowledge of fundamental scientific principles and methods to appreciate the helpfulness of technical research. The Pratt Institute at Brooklyn is fully alive to this demand and has shaped its courses admirably to meet it.

The steel industry in its many ramifications promises an immense amount of research, ranging from the most refined studies in metallography to experimentation upon the gigantic scale required for the development of the Gayley dry blast, the Whiting process for slag cement or the South Chicago electric furnace. This furnace has probably operated upon a greater variety of products than any other electric furnace in the world.

Coal-Tar Color Chemistry.

The Textile Mercury of Manchester, England, reports additional facilities for the training of industrial chemists have been provided in a new department for specialized study and research in coal-tar color chemistry, established by the governors of the Huddersfield Technical College, with the approval of the Huddersfield town council. The department has been placed under the direction of an expert, who has been carrying out a series of important investigations on colors and plant pigments. Work will begin in September and the department will provide advanced teaching in matters relating to the production of dyestuffs, colors, and allied substances. Facilities will be offered for research of all kinds relating to the chemistry of coloring matters, and the department will be conducted in close connection with the existing departments of chemistry and dyeing.

In addition to day classes for students able to devote the whole of their time to such work, special attention will be given to the training in part-time day and evening classes of youths and men already engaged in the industry.

The directors of British Dyes (Ltd.) are supporting the plan, and the Mercury states that they are prepared to contribute substantially toward the project. At Leeds University there is already a department of color chemistry and dyeing, the endowment of which was provided by the Clothworkers' Co.

NOTE ON THE APPLICABILITY OF THE PAPER PULP FILTER TO THE SEPARATION OF SOLIDS FROM LIQUIDS.*

By S. L. JODIDI, Ph. D.†

INTRODUCTION.

Of the materials used in analytical work for the separation of liquids from precipitates, filter-paper and asbestos are the best known, while filters of cloth, wool, cotton, silk, etc., are ordinarily employed in work other than analytical. Whereas, paper pulp may have been used in a few cases for special purposes, it is noteworthy that the pulp filter, which has been shown by E. H. Kellogg and the writer to be generally applicable to quantitative¹ analysis, is—so far as we are aware—not even mentioned in voluminous text-books of analytical chemistry, such as Fresenius,² Treadwell,³ Hoppe-Seyler,⁴ and others. Even in Abderhalden's up-to-date "Handbuch der biochemischen Arbeitsmethoden," made up of not less than ten volumes with a total of about eight thousand pages, the paper pulp⁵ is mentioned in but three sentences. In the Handbuch, however, the pulp is not as such recommended for the filtration of fine precipitates, like barium sulphate, but in connection with paper filters.

IMPORTANCE OF A GOOD FILTER FOR ANALYTICAL WORK.

The analytical chemistry is largely based upon estimation of precipitates. While volumetric, acidimetric, and, especially, colorimetric and nephelometric⁶ methods are coming more and more into use, the quantitative and qualitative analysis is still, in most cases, dependent upon the determination of precipitates. Of all operations necessary to quantitatively obtain the precipitates in a pure form, their filtration through filter-paper is one which is not only very tedious and time-consuming, but requires also certain skill. That filtration (including decantation) takes a considerable part of the time necessary for an analysis every chemist knows from his own experience, and is also evident from the fact that the text-books of analytical chemistry usually devote much space and painstaking details to the processes of decantation, filtration, and washing of precipitates. It is, therefore, quite advantageous to make use of the pulp filter, which, in connection with a research into the chestnut⁷ bark disease, was shown to be applicable to the estimation of phosphorus,⁸ calcium,⁹ and mag-

*From the July Journal of the Franklin Institute.

†Office of Plant Physiological and Fermentation Investigations, Bureau of Plant Industry, U. S. Department of Agriculture.

¹Jodidi, S. L., and Kellogg, E. H., Jour. Ind. and Engin. Chem., 8, 317, 1916.

²Fresenius, "Quantitative Analysis," vol. 1, p. 88, 1903.

³Treadwell, "Analytical Chemistry," vol. II, p. 16, 1907.

⁴Hoppe-Seyler's "Handbuch der Physiol.-Pathol. Chem. Anal.," p. 5, 1909.

⁵"Handbuch der biochemischen Arbeitsmethoden," by Emil Abderhalden, vol. 1, 98.

⁶Kober, P. A., and Egerer, G., Jour. Amer. Chem. Soc., 37, 2573, 1915; Kober, P. A., and Graves, E. E., Jour. Ind. and Engin. Chem., 7, 849, 1915; S. S. Graves and P. A. Kober, Jour. Amer. Chem. Soc., 37, 2420, 1915.

⁷S. L. Jodidi, Jour. Amer. Chem. Soc., 37, 1708, 1915; S. L. Jodidi and E. H. Kellogg, Jour. Franklin Institute, 180, 349, 1915.

⁸S. L. Jodidi and E. H. Kellogg, Biochemical Bulletin, 5, 87, 1916.

nesium,⁹ and to quantitative¹⁰ analysis in general. The pulp filter permits of comparatively rapid filtration and washing, so that one is able to save considerable time and labor. A simple consideration will show why this filter permits of rapid work, combined with economy and accuracy.

RAPIDITY.

The actual filtration through an ordinary paper-filter, because it snugly rests on the walls of the funnel, takes place chiefly through a very small portion only; namely, through its conical part, which freely hangs over the stem of the funnel. As the filtration goes on, this free filtering part is gradually plugged up, which more and more retards the filtration. On the other side, the filtration on the pulp filter, whether used with a Gooch crucible or with a perforated plate, takes place through a number of holes (usually from 60 to 70), so that when some of them are plugged up during filtration the others still continue to filter well. But what seems to be of greater importance is the fact that the work with the paper pulp filter enables one to make use of suction, which, as in the case of the asbestos filter, considerably accelerates the rapidity of the filtration.

The direct experiment shows (which seems also evident) that, *caeteris paribus*, the thicker a pulp filter is, the more slowly it filters, and *vice versa*. By using, however, pulp emulsion of equal consistency—from

1.5 to 2 c.c.¹¹ of water for each centigramme of filter-paper—and by preparing the pulp filters in a definite way it is fairly easy to obtain filters of uniform thickness and efficiency.

To illustrate the rapidity of filtration through a pulp filter, as compared with an ordinary paper filter, it seems worth while here to arrange a few previous data in tabular form.

ACCURACY.

For analytical purposes the accuracy of an ordinary paper filter, though half of it is threefold, is the accuracy of which just one filter layer is capable, because the other half of an ordinary filter is but single-folded. The pulp filter, on the other hand, has a manifold filtering surface, as can be seen from the following consideration. An 11-cm. filter, *e. g.* (frequently used in quantitative analysis), has a total filtering surface of 95 sq. cm., whereas a Gooch crucible (with a bottom of 2.22 cm. in diameter) has 3.87 sq. cm. of filtering surface. Hence, by using the reduced pulp of an 11-cm. filter for five Gooches, the filtering surface of the pulp filter can be made up of four or five layers. While this is not uniformly the case throughout the filter, its weakest part may safely be assumed to have not less than two or three layers. For this very reason the filtrates from pulp filters are, as a rule, much clearer than those from paper filters and comparatively seldom need refiltration.

ECONOMY.

The above calculation shows that the pulp of a filter of 11-cm. diameter is sufficient for four or five Gooches, *i. e.*, for four or five quantitative analyses, which stands in agreement with the direct experiment.

Precipitate.	On paper filter, minutes.	On pulp filter, minutes.	Remarks.
Ammonium phosphate ¹²	20-35	5	The paper filter used was an S. & S. folded filter, No. 588, of 12½ cm. diameter.
Calcium oxalate ¹³	30-35	5	
Magnesium ammonium phosphate ¹⁴	30	3-6	The paper filter employed was an S. & S. filter, No. 590, of 9 cm. diameter.
Barium sulphate ¹⁵	35	10	The same paper filter was used as in the case of magnesium ammonium phosphate.
Silver chloride	30-40	8-15	The same paper filter was used as in the case of magnesium ammonium phosphate.
Potassium platonic chloride	40-50	15	The same paper filter was used as in the case of magnesium ammonium phosphate.

Paper filters used	Diameter of filter, cm.	Economy of filter paper obtained by reducing the paper filters to pulp, per cent.	Diameter of filter, cm.	Economy of filter paper obtained by reducing the paper filters to pulp, per cent.	Diameter of filter, cm.	Economy of filter paper obtained by reducing the paper filters to pulp, per cent.
S. & S., No. 588, folded ¹⁶	9	166	11	248	12½	320
S. & S., No. 595 ¹⁷	9	201	11	300	12½	387
S. & S., No. 589	9	190	11	284	12½	367
S. & S., No. 598	9	300	11	448	12½	579
Commonest sheet filter paper	9	313	11	467	12½	603
Average	..	234	..	349		451

This fact will readily be comprehended when we consider that at most half of an ordinary paper filter can for analytical purposes be utilized, since half of it is threefold. As the filter, however, is never filled to its upper edge, it is fair to state that from two-thirds to three-quarters of the ordinary paper filter is

⁹S. I. Jodidi and E. H. Kellogg, Jour. Franklin Institute, 181, 217, 1916; Chemical Engineer, 23, 60, 1916.

¹⁰S. I. Jodidi and E. H. Kellogg, Jour. Ind. and Engin. Chem., 8, 217, 1916.

¹¹Not published yet.

¹²Jour. Franklin Institute, 181, 222, 1916.

¹³Ibid., 181, 229, 1916.

¹⁴Jour. Ind. and Engin. Chem., 8, 218, 1916.

¹⁵The details will be published in Biochemical Bulletin, 5, 87-94, 1916.

¹⁶Jour. Franklin Institute, 181, 231, 1916.

¹⁷S. & S. filters, Nos. 589 and 588, of 12½ cm. diameter, weigh about 0.55 and 0.8 gr., respectively. Equally, an S. & S. filter, No. 595, of 11 cm. diameter, weighs about 0.6 gr. The weight of an 11-cm. filter of common sheet filter-paper was found to be 0.75 gr. The average weight of one filter of the above descriptions—frequently used for analytical work—is about 0.75 gr., which, reduced with some 150 c.c. of water (2 c.c. water to 1 centigramme paper), gives a paper pulp which is ordinarily suitable for analytical and other purposes.

wasted, whereas the filtering surface of the pulp filter is fully utilized.

For the sake of convenience the results in question recalculated to filters of 9, 11, and 12½ cm. diameter, respectively, are presented in Table II.

Table II shows that when paper filters of 9, 11, and 12½ cm. diameter, respectively, are reduced with water to pulp, there results an average economy of filter-paper amounting to 234, 349, and 451, respectively, the total average being 345 per cent. This is the arithmetical expression of the experimentally-demonstrated fact that one quantitative paper filter of average thickness and size, when reduced with water to pulp, yields enough of it to cover about four Gooch crucibles with pulp filters.

THE PAPER PULP FILTER AS COMPARED WITH OTHER
FILTERS GENERALLY EMPLOYED IN QUANTITATIVE
ANALYSIS.

So far as quantitative analysis is concerned, good filter-paper was preferably used for the separation of precipitates from liquids. It is perfectly true that the Gooch¹⁸ asbestos filter is extensively used in analytical work, since it offers several advantages, chief among which is the rapidity and accuracy of work, as well as the possibility of using the same asbestos filter for several consecutive determinations. But it is true, also, that, in addition to the asbestos filter, the ordinary paper filter is still employed to a great extent in analytical, synthetical, and other work. Yet it is a matter of common knowledge that paper filters, far from being a quick filtering medium, yield not infrequently turbid filtrates or even break during filtration, which necessitates repeated refiltrations. On the other hand, the pulp filter, which never breaks and permits of uniform and comparatively rapid work, gives, as a rule, clear filtrates. For these and other reasons outlined above, the paper filter should be replaced by the pulp filter, wherever possible, since the latter offers many advantages. It retains¹⁹ fine precipitates, such as ammonium phosphomolybdate, calcium oxalate, etc., more readily than a paper filter or a new asbestos filter. It is more accessible, easier to handle, and requires less time and skill for its preparation than the asbestos filter. The work with the pulp filter is more convenient and more rapid than with the paper filter. The fact that the use of the pulp filter enables one to make considerable saving of filter-paper is at present especially significant in view of the scarcity of good filter-paper in this country.

WHEN IS THE PAPER PULP FILTER APPLICABLE?

We had already occasion to indicate as to why the pulp filter is preferable to either the paper filter or asbestos filter. As to the applicability of the pulp filter, it may generally be stated that it is applicable

wherever the ordinary paper filter can be used. Thus it was demonstrated in previous papers²⁰ that the pulp filter can be used for the quantitative estimation of the acids—phosphoric, hydrochloric, sulphuric; and of the bases—potassium, ammonium, barium, calcium, magnesium, silver; and for quantitative analysis in general. It is a matter of course that it can be applied also to qualitative analysis, to preparation work, or wherever crystallized or more or less crystalline precipitates have to be separated from neutral or moderately acid and alkaline liquids. The paper pulp filter, however, should not be used for the filtration of strongly acid or alkaline liquids (which holds also true for the ordinary paper filter), in which case filters of asbestos or glass wool are preferable; nor should the pulp filter be used for separation of colloidal substances.

For the filtration of very small precipitates—from a few milligrammes down to one milligramme or less—contained in a small volume of liquid, the common paper filter of small size may in some cases be preferred. Especially will this be the case whenever it is essential to have the substance absolutely free from paper fibre. On the other hand, the pulp filter will render very good services for the refiltration of considerable quantities of not quite clear liquids, or for the separation of comparatively large quantities of liquids from small precipitates.

It may be emphasized here that whether a single analysis or series of them are to be made, the pulp filter offers distinct advantages, because it enables one to accomplish the work in less time with less filtering material and with just as accurate results as can be obtained with good paper filters.

CONCLUSIONS.

1. The reasons are outlined in detail as to why the pulp filter (whenever applicable) is superior to the paper filter and asbestos filter—the economy of filter-paper, rapidity and accuracy of work, and easy accessibility being the most important factors involved in the use of the pulp filter.

2. The instances are definitely stated as to when the pulp filter is applicable, or is to be used in preference to either the paper filter or asbestos filter.

A compilation of wholesale sugar prices as of Aug. 1 at all the principal consignment points throughout the country, which has been made by the Federal Sugar Refining Company, discloses the fact that the citizens of the Western section of the United States, the home of the sugar beet industry, pay more for their sugar than those who live in the East and consume the foreign grown varieties.

Twenty-one Western communities, including San Francisco, Denver, Kansas City, Seattle and Detroit, show an average wholesale price of 8.136 cts. a pound, as against 7.80 cts. for twenty-one cities in the Eastern section. Helena, Mont., pays the highest figure in the country, 8.65 cts. a pound.

¹⁸Jour. Amer. Chem. Soc., 12, 45 (1883); Ber. Deutsch. Chem. Ges., 32, 2142 (1899). See also Munroe crucible, Jour. Analyt. Chem., 2, 241 (1888); Chem. News, 58, 101 (1888).

¹⁹That precipitates like calcium oxalate, barium sulphate, and ammonium phosphomolybdate frequently pass through filter-paper is so well known a fact that we here need not dwell upon it. See, in this connection, S. L. Jodid and E. H. Kellogg, Jour. Franklin Institute, 181, 228, 1916, footnote; Biochem. Bulletin, 5, 87-94, 1916.

ELECTROLYTIC PRODUCTION OF HYDROGEN.*

By HARRY L. BARNITZ, PH.G.†

There has been followed by every advancement in the generation of electric currents a great extension of the uses of electricity. The rapid growth in the last few years of power plants for generating electricity and the low cost of production has been accompanied by the development of electrochemical processes for the manufacture of materials formerly prepared in other ways; by the application of electrical methods to the extraction and refining of metals; and by the separation of elements and the production of new compounds, which electrical processes alone can effect. One of the more important relations between electricity and chemical action is the production of hydrogen.

It is not my purpose to go into past history regarding the earlier and various stages of development of the generating apparatus used for the electrolytical production of hydrogen, but to describe the method of production of hydrogen by one of the most recent and efficient electrolytic generating apparatus, known as electrolytic cell or generator as now used in the technical production of this important gas. The function of the electrolytic cell or generator is, by the aid of electricity, to separate water into its elements, hydrogen and oxygen.

Two types of generators are used, the unit and the filter press. The former I will take up first:

This type of cell is installed at the U. S. Navy Yard at Brooklyn, Edison Storage Battery Co., Westinghouse Lamp Co., Cooper Hewitt Electric Co., General Electric Co., and many other large corporations. The total number of the unit type installations made is considerable in excess of 50, with a yearly generating capacity of many hundreds of thousands of cubic feet of hydrogen.

The various parts of the unit type cells are:

Insulating supports.

Diaphragm (in special perforated sheet metal and asbestos sacks which permits ions to pass freely but prevents the mixing of the bubbles of liberated gases and it is the positive electrode on which the oxygen is generated).

Hydraulic joint (prevents the mixing of the liberated gases).

Filling cup.

Negative electrode terminals (the iron tank serves as negative electrode—hydrogen is generated on inside).

Positive electrode terminals (also supports the diaphragm).

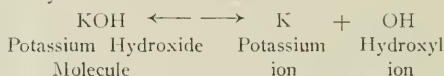
Indicator and pressure equalizer (delivers the gases at constant pressure).

Hydrogen offtake, Oxygen offtake—to gasholders for compressing into cylinders.

The general dimensions are:

Height of cell 2 ft. 10 ins., height over all 5 ft. 6 ins., length over all 3 ft. 9 ins., width over all 1 ft. 9 ins., weight when empty 1,000 lbs., weight full of 1,500 lbs.

In each cell there is placed 100 lbs. of soda or 165 lbs. potash, which, when water is added, forms the electrolyte. It is not necessary to replenish the soda or potash. This is explained chemically by the dissociation theory—which is when electrolyte is dissolved in water, a portion at least of its molecules break up into two parts one charged with positive electricity, and the other with an equal amount of negative electricity. The charged portions of the molecule are called, respectively, positive and negative *ions*. Thus, if we take as the electrolyte, caustic potash, the first action is in the electrolysis, the dissociation of potassium hydroxide when it dissolves:

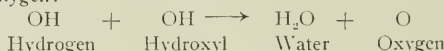


When the potassium *ion* reaches the negative electrode, it loses its charge, becomes a potass, atom, and reacts with the water of the solution, forming potassium hydroxide again and liberating hydrogen:



Potassium Water Potassium Hydroxide Hydrogen

The hydroxyl ions, when they lose their charges, react with each other, forming water and liberating oxygen:



It will be seen the net result of these actions is the removal of one molecule of water from the solution and the liberation of two atoms of hydrogen and one atom of oxygen. So it will be seen that water in the cell only needs to be renewed and not the potassium hydroxide. The amount of water used is a little less than 1 gallon in 24 hours.

The generators when operating at about 30° C. with 28.9 per cent KOH solution will average at least 8 cu. ft. of hydrogen and 4 cu. ft. of oxygen per KWH, and at least 6.3 cu. ft. of hydrogen and 3.2 cu. ft. of oxygen per clock hour, measured at 20° C. and 760 MM. pressure when operating with 2 volts by 400 amperes D.C.

Purity of gases direct from the generators—hydrogen 99.5 per cent or better, oxygen 99 per cent or better.

The features of the unit type generator referred to are:

(a) That the unit type generator produces the maximum quantity of pure hydrogen and oxygen simultaneously per KWH that can be produced, and at a minimum cost for upkeep.

(b) It is so designed that by means of a special device called the hydraulic joint, any explosive mix-

*Paper read before The Aeronautical Society of America and printed in the May-June Journal of the Society.

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ture of the gases is prevented. In addition the sight feed indicators show whether the generator is functioning properly while the pressure equalizers counter-balance any excess pressure.

(c) A cell of this construction is practically indestructible. The parts are selected, manufactured and designed free from any perishable materials. There are no moving parts to get out of order. Generators installed in 1900 are still in operation.

(d) The generators require no expert attention. As soon as the switch is turned on the gases begin to bubble through the sight feed indicators; as soon as the current is shut off, the production ceases. Generators can be operated continuously twenty-four hours a day every day in the year—there is no need to stop the plant for cleaning or overhauling.

(e) The generators produce the same quantity of gases of the same purities right along. The gases are of uniform high purity, unless some unusual condition prevails. The reports covering long periods in the operation show variation in the purity of hydrogen and oxygen not exceeding two-tenths of 1 per cent.

(f) The only attention the unit type generators require is the addition of the necessary amount of distilled water daily. In many plants the operating charge for labor does not exceed the cost of one or two hours of one man's time per day.

I will now take up the filter press type hydrogen and oxygen generator. This is the type of generator installed at the plant of the U. S. Naval Aeronautic Station at Pensacola, Fla. The fundamental principle of the unit type generator is embodied in the filter press type generator—the only change made is in the mechanical construction of the filter press type generator. It has distinct advantages for certain operating conditions over the unit type. Its principal feature is—maximum capacity in minimum space. Two size generators are made—the dimensions of the small size are 2 ft. 6 ins. wide, 12 ft. long and 8 ins. high, containing 60 bipolar plates 18 ins. square with a voltage drop per plate of 2 volts and with a total voltage per generator 120 volts by 80 amperes D.C.

(1) Capacity of hydrogen generated per hour 70 cu. ft.

(2) Capacity of oxygen generated per hour 35 cu. ft.

(3) Capacity of hydrogen generated per 24 hours 1,680 cu. ft.

(4) Capacity of oxygen generated per 24 hours 840 cu. ft.

The large size generators have dimensions of 4 ft. 6 ins. wide, 14 ft. 6 ins. long, and 8 ft. high, containing 60 bipolar plates 36 ins. square with a voltage drop per plate of 2 volts and with a total voltage of 120 volts by 320 amperes D.C.

Capacity on large generators,		
Hydrogen	per hour	280 cu. ft.
Oxygen	"	140 "
Hydrogen	" 24 hours	6720 "
Oxygen	" 24 "	3360 "

Efficiency is identical in both sizes when operating at about 70 degrees C (which is normal temperature) with 28.9 per cent K.O.H solution each generator will give at least

(1) 7.5 cu. ft. hydrogen,

(2) 3.75 cu. ft. oxygen

per K.W.H. the gases to be measured at 20° C., 760 mm. pressure—400 lbs. soda or 800 lbs. potash will be required to produce the electrolyte.

Purity of the gases direct from the generator—hydrogen 99.9 per cent; oxygen 99.8 per cent.

The filter press type generator consists mainly of a series of metallic plates (electrodes) clamped up together and supported in a heavy frame, electrically insulated from one another, and separated by diaphragms of porous fabric. Each pair of these electrodes forms a closed cell, divided by the diaphragm. These cells are filled with the electrolyte (an aqueous solution of caustic potash or soda) which acts as a conductor connecting up the plates in series.

An electric current admitted at one end plate passes on through the plates and through the solution to the other end plate. In its passage, it decomposes the water in the solution into the two gases—hydrogen and oxygen—which are released on opposite sides of each plate and emerge upward into the gas off-takes. The mingling of the hydrogen and oxygen in each cell or compartment is prevented by the diaphragm which, while permitting the passage of the fluid, resists the passage of the gases, according to a well-known physical law.

As the gases are released and withdrawn, the distilled water is automatically replenished from a supply tank. The operation is continuous so long as current is supplied and electrolyte maintained.

In the smaller machine, the electrodes are carried on two steel rods supported on two heavy end pieces or pedestals of cast iron. In the larger generator the side rods are replaced by deep steel bars. The construction is one of extreme rigidity, absolute proof against any distortion and consequent disarrangement of electrodes; with resultant leakage. The electrodes are clamped together by a heavy screw working in the rear support. A feature of special note in the filter press generator is that a ball thrust bearing is interposed between the end of the clamping screw and the rear end plate—which contributes to the non-leaking qualities of the machine by doing away with the tendency of the electrodes to "ride up" from the side bars under screw pressure.

The electrodes are of special design and are composed of special alloy—covered by patents. The anode side being heavily nicked which materially facilitates the electrolysis or decomposition, and to lower the voltage, while the cathode side is of iron. Incidentally these by-metallic electrodes prevent the formation of rust and oxides which would eventually shorten the life of the apparatus. The surface

of the electrodes carry vertical corrugations which are interrupted by a large number of depressions to facilitate the flow of the electrolyte into the cell and the release of the gases from it.

At top and bottom of each electrode are two openings communicating by cored channels with opposite sides of the plate. Those at the bottom are for the water intakes and those at the top are for the gas off-takes. It will be seen that each half of each cell (separated by the diaphragm) has its own independent water intake and gas outlet, so that there can be no possibility of the two gases mingling through these channels. Any gas leakage which may occur between the electrodes escapes to the open air and not into the adjacent cell or into the gas off-takes.

These are of specially prepared asbestos fabric of a thickness and texture carefully worked out by long experience and experiment to give the best results. All around the edge of this fabric is molded a packing rim of pure rubber which is an integral part of the diaphragm and which rests in a recessed groove on the face of the electrode.

In a generator of this type an essential of power economy is that all the current supplied the machine shall pass through the electrolyte and none of it be by-passed through the metal of the machine or through the water inlet and gas outlets.

In the filter press type generator, the electrodes are insulated from the side bars of the frames by porcelain insulators resting on a wooden bar in the large machines and on fibre in the small machines. They are insulated from one another: first, by the pure rubber packing rim surrounding the diaphragms, second by nipples of pure rubber inserted in the water intake and gas off-take shoulders of the electrodes—these nipples, with everything clamped home, meeting one another and not only insulating the electrode shoulders but also providing an insulating tube in the interior of the water intakes and gas off-takes.

The gases rising from the electrodes and entering the gas off-takes carry with them a small percentage of the electrolyte, which if allowed to enter the external piping system would ground the apparatus.

To guard against this contingency, there is provided in each gas off-take a special system of insulating sections—each consisting of two heavy glass tubes clamped between flanged drain sections so devised as to intercept and withdraw through an insulating connection the moisture entrained in the gases. The gases emerge through these insulators substantially dry and free from electrolyte.

Not only do these insulating connections prevent grounding and waste of current. They also permit two more generators to be operated in series, instead of in parallel, with the advantage of keeping the production the same in each generator without the use of devices for cutting out electrodes or introducing resistance in the circuit. Each generator is independent of every other in the system.

The two important features in electrical efficiency in this type generator are—first, the composition alloy and nickel plating used in the manufacture of the electrodes. Second, that the design of this generator is such as to retain within the apparatus most of the heat produced as a result of the ohmic resistance. This keeps the electrolyte and the electrodes at a comparatively high temperature, which adds to the efficiency of the electrolytic process. Furthermore, the electrolyte used—a solution of caustic soda or potash—has been found by experiment to utilize the current to best advantage.

Before starting the apparatus the generator is filled with the solution of electrolyte as the decomposition proceeds and gases withdrawn, water must be supplied to the solution to maintain the right density. On the front of the generator and elevated above the electrodes, is a solution box or tank which receives the distilled water that is supplied to the electrode chambers or cells. From this tank a pipe descends to a water-feed manifold, the latter branching to two independent connections to the two separate water intakes to the cells. And from this manifold two risers lead, one to each of the two gas domes above.

Into these gas domes the oxygen and hydrogen are separately introduced as generated—the discharge taking place through an inverted “L” below the fluid level in the dome. This level is determined by—or is a resultant of—the static pressure due to the fluid in the solution box, and the gas pressure. The arrangement is such that the fluid level between the electrodes is automatically maintained at the proper point, at all times. And the rate of water feed is absolutely proportioned to and determined by the rate of gas generation.

A primary essential in a generator of this type is to minimize circulation through the diaphragms—the function of these diaphragms being only to segregate the two gases as released, at the same time permitting contact of the electrolyte through their pores.

The two independent water supplies—one to either side of each diaphragm, but both under exactly the same pressure due to the hydrostatic head between the electrodes—obviously put the diaphragms under balanced fluid pressure, and eliminate circulation through and over them due to unequal pressure on their two sides.

This has two vital results. First, it removes any tendency to cause a mingling of gases through the diaphragm. Second, it relieves the diaphragm material from all mechanical stress and obviates any destructive erosive action which might be caused by solid particles in the electrolyte being forced over or through the fabric. This absolute balance and control of water pressure, then, affects both the purity of the gases and the life of the apparatus.

The two gas off-takes discharge into the two independent gas domes already referred to, the gas emerging below the fluid surface through an inverted “L.”

It is apparent, then, that the pressure on both gases, clear back to the individual cells, is the same—being that determined by the position of the inverted “L” in the fluid and by the hydrostatic head in the solution tank.

These balanced pressures in both gas off-takes forbid any mixture of the gases and contribute to the balancing of pressures on the diaphragms. It will be noted that gas and water pressures are predetermined and constant.

The gases, escaping from the gas off-take “L’s,” rise through the fluid in the gas domes and pass out through the gas discharges at the top of the domes—thence downward to purgers on either side. These purgers are closed boxes of cast iron filled with water to a certain level. The gases escape below the surface of this water, pass upward through it and emerge thence to the supply lines and to the gasholders.

The function of these purgers is three-fold: first, to catch any entrained fluid in the gas; second, to cool the gas; third, to act as a water-check-valve protecting the pressure system of the generator from any external variation or excess of pressure. Furthermore, each generator is thus made independent of every other in the plant.

A signal whistle is provided which gives notice when the level of the solution of the generator falls below the prescribed limit. Glass sight-feed indicators on the solution tank and gas domes show the fluid levels and reveal the generation of the gases. Gauge glasses connecting with the electrodes at intervals along the generator show the fluid levels in the body of the apparatus.

To permit the emptying of solution from the generator when required, drain valves are provided. These are of the lever-operated gate type, designed to obviate any leakage or wear due to the presence of solid matter in the fluid.

The only parts subject to deterioration and replacement are the rubber of the insulating nipples and diaphragms packing rims. Observations on this pure rubber insulation during the years of experimental work on this generator, demonstrate that it has a length of life highly satisfactory. The asbestos fabric of the diaphragms has been proved to be strong and durable—and it has already been pointed out that mechanical deterioration of the fabric is minimized by the balancing of pressure and the reduction of fluid circulation within the apparatus. The up-keep cost on the filter press type generator has been reduced to the practical limit.

It is as completely automatic as a high-duty device can be made. Practically the only attention required in operation is a maintenance of the water supply, and calls only for a minimum of attendance—at the most, only a small part of one man's time. And this feature contributes largely to the low cost of gas production to be realized by this apparatus.

OCCUPATIONAL DISEASES.

At the meeting of the American Chemical Society in New York on Sept. 25 to 30, there will be conducted a symposium on Occupational Diseases, presided over by Professor Charles Baskerville, head of the department of chemistry of the College of the City of New York. The subject is interesting and important as well as full of surprises. Housemaid's knee, for instance, which for many years has served as a subject for humorous comment, proves to be a frequent malady of miners. The statistician is abroad in this and other lands and he brings the information that trades carried on in the presence of much dust show a high death rate from diseases of the lungs. Then comes the biologist who explains that dust is not only minute particles, but that the particles are usually surrounded by a watery envelope, and that clinging to this filament there may be micro-organisms.

The medical authorities abroad declare that soot is a serious irritant and that chimney-sweeps are especially subject to cancer because of it. Sawing certain kinds of wood has been found to produce irritation of the mucous membranes of the nose, throat and eyes. The makers of white lead have looked lead poisoning square in the face and have found means to avoid it. Dr. Patterson of Philadelphia devised an entirely reasonable but somewhat unexpected treatment for it. He immerses the patient's hands in one tub of salt water and his feet in another, and then a pole of an electric battery is put into each of the tubs. The current is turned on, using Mr. Patient as a conductor, and it carries the lead that it finds on the way, out of him, through the salt solution and deposits it upon one of the electrodes. It has proved successful.

Fatigue is another subject that has been studied and reported on. Strain is declared to be more exhausting than work, and monotony of employment aggravates exhaustion. Fatigue seems to be a condition of the body in which the waste products of work are not carried off fast enough. In physiological laboratories animals have been fatigued by over-driving and then some of their blood has been injected into the veins of healthy animals. The healthy animals straight-way showed the same symptoms of fatigue as those that had been over-worked.

In rubber factories and elsewhere, when bisulphide of carbon is used, great care must be taken to avoid contamination of the air by its offensive fumes. Otherwise nervous troubles are likely to follow.

There is bakers' itch, grocers' itch and sugar refiners' itch, all manifestations of eczema, according to the materials handled.

The question is likely to be asked why boards of health do not use chlorinated water for flushing the streets, especially in hot, dry weather. This was first proposed by Dr. Baskerville six or seven years ago, and there is no question but that its effect upon disease germs in the street dust would be beneficial to the

public health. Since the New York water supply has been treated with chlorine, not a single case of typhoid fever has been traced to it as the cause. It is doubtful if any other satisfactory answer will be forthcoming than that the boards of health haven't got around to it yet.

The symposium will consider the chemical trades, prophylaxis in chemical industry, diseases incidental to work in aniline and other coal tar products, cedar lumber, mines, explosives, and a general discussion by the leading authorities of the country. These will include Drs. W. Gilman Thompson, F. L. Hofman, J. W. Schereschewsky, G. P. Adamson, H. K. Benson, W. A. Lynott, Alice Hamilton and Mr. J. B. Andrews.

Alcohol-Benzol Mixture as Motor Fuel.

Among the many efforts made by Germany to counteract the effects of a blockade, one of special interest is the replacing of gasoline for automobiles by a mixture of alcohol and benzol. With the cessation of imports of gasoline into Germany the supplies of petroleum drawn from wells in Galicia proved inadequate for the needs of the Central States. For this reason, the German Government instructed the technical department of the transportation service to seek a combustible that would effectively replace gasoline. The outcome of these experiments was the employment of a mixture of alcohol and benzol. A Mercedes car of the 1914 touring model, having an ordinary carburetor, was used for experimenting purposes, with the following results:

Fuel.	Speed per hour (miles).	Distance covered on 1 pint of fuel (miles).
Alcohol-benzol mixture:		
1 part benzol, 1 part alcohol	42	4.66
1 part benzol, 2 parts alcohol	41	4.47
1 part benzol, 3 parts alcohol	39	4.34
1 part benzol, 4 parts alcohol	38	4.10
1 part benzol, 5 parts alcohol	36	3.72
Benzol, pure	42	3.79
Gasoline, pure	44	3.60

ECONOMY OF NEW FUEL.

Even if the alcohol be figured at before-the-war prices the use of such a mixture is an economy. One pint of gasoline costs 8.55 cents, benzol 8.17 cents, and alcohol 7.79 cents.

There remained, however, a serious drawback in connection with this mixture, and that was the difficulty in starting the automobile. This was overcome by installing on each car a small supplementary reservoir containing gasoline, benzine, or ether, which is drawn upon when starting the car, and the alcohol-benzol fuel then substituted.

According to a Daily Commerce Report, from which this note has been taken, Germany now makes current use of this mixture, which is readily manufactured by distilling beets and coal tar, both of which products abound in that country.

TREATMENT OF PACKING-HOUSE SEWAGE BY AERATION IN THE PRESENCE OF ACTIVATED SLUDGE*

By PAUL RUDNICK and G. L. NOBLE.†

This paper is a brief account of experiments with the activated-sludge process on sewage from the plant of Armour & Co., at Chicago.

An idea of the extreme variation in the nature and composition of the different kinds of sewage involved may be obtained from the following list of the more important departments where this sewage originates: Hog, beef and sheep abattoirs, power plant, lard refinery, oleomargarine, meat-canning, meat-curing and sausage departments, rendering tanks, fertilizer plant, several other smaller departments, and the domestic sewage of 10,000 employees. This sewage is much more concentrated than domestic sewage, containing approximately four times as much suspended solids. Averages of recent analyses, including analyses of night and holiday sewage, show the composition in Table 1. The suspended solids consist largely of organic material. The high content of inorganic matter is caused to great extent by the deep-well water used in many departments, the total solids of which is more than 2,000 parts per million.

TABLE 1—SOLIDS IN RAW SEWAGE: PARTS PER MILLION.

Organic	560	Organic suspended solids.425
Inorganic	2,990	Inorganic suspended solids 75

Total3,550 Total suspended solids..500

Sewage from each of the three main outlets is pumped into a weir box, which also acts as a small grit chamber. From this the sewage passes into an aerating tank 10 ft. by 20 ft. by 10 ft., where it is aerated for 10 hours. A partition is arranged so that the path of the flow is about 40 ft. long. Sludge containing 99.5 per cent water, which has been aerated for 3 hours, is introduced into the aerating tank at the same point as the raw sewage at the rate of 30 per cent of the raw sewage flow. The aerating tank is fitted with underflow and overflow baffles, and the air is distributed by means of 3/4-inch pipes perforated with 1/25-inch holes, 2 ins. apart and staggered, the pipes being placed at 4-ft. intervals at right angles to the line of flow. After leaving the aeration tank the sewage is allowed to settle 40 to 60 min. in a separate chamber. The sludge is siphoned continuously into the sludge storage and the effluent continuously flows over the edges of the settling chamber. The air is measured by means of an orifice and differential manometer; 3 cu. ft. of air are required per gal. of sewage. This includes the air used for siphoning the sludge from the settling chamber to the sludge storage and from the sludge storage to the aerating tank for inoculation. The effluent is fairly clear and practically odorless. The methylene blue test¹ shows that

*Paper presented at Urbana-Champaign meeting of the American Chemical Society.

†Chief Chemist and Chemist, Armour & Company.

it is nonputrescible for at least 4 days. Typical sanitary analyses of the effluent are shown in Table II.

TABLE II—NITROGEN CONTENTS OF EFFLUENT: PARTS PER MILLION.

Albuminoid.	Ammonia.	Nitrite.	Nitrate.
2.40	23.80	0.60	None
7.40	16.20	0.97	None
3.00	31.20	0.25	None
4.10	27.90	0.15	None
2.50	28.60	Trace	None

The change in the composition of the sewage caused by the aeration process is concisely shown in Table III, which gives the percentage of decrease of certain constituents.

TABLE III—APPROXIMATE PERCENTAGE REDUCTION OF CERTAIN CONSTITUENTS BY AERATION.

Albuminoid nitrogen.	Ammonia nitrogen.	Total organic nitrogen.	Total organic matter.	Suspended solids.
96	71	66	70	95

A very important factor in the decomposition of the sludge is its high content of moisture and the difficulty of dewatering it in large quantities. A summary of a series of analyses of sludge obtained from

TABLE IV—ANALYSIS OF SLUDGE: RESULTS IN PERCENTAGES.

No. of analyses.	Moisture	Ammonia (a)	Nitrogen (a)	Fat (a)
12.	18.	18.	18.	17.
Maximum	99.70	7.84	6.46	9.36
Minimum	99.10	3.60	2.96	1.98
Average	99.48	5.57	4.59	5.54

(a) Calculated to a commercially dry (10 per cent moisture) basis.

the experimental unit is given in Table IV, which shows also the limits which may be expected for the fertilizer value and the fat content of the dried sludge.

The dry sludge contains very small proportions of phosphoric acid (approximately 2 per cent calculated as P_2O_5) and potash (approximately 0.4 per cent calculated as K_2O) and its fertilizer value therefore lies entirely in its content of nitrogen.

Much work has been done to find some practicable means of dewatering the sludge so that it may be obtained in a form in which it can be dried in the driers regularly used for handling fertilizer materials. The moisture content of the wet sludge coming from the settling chamber must be reduced from 99.5 to 50 per cent if possible. The importance of this problem is brought out much more clearly when it is considered that such reduction involves the removal of almost 99 per cent of the weight of the wet sludge as it comes from the settling chamber.

Filter pressing in the ordinary type of filter press and in the newer forms, such as Kelly or Sweetland presses, has proved entirely unsuccessful. The filter cloths are very rapidly clogged. A special type of filter press may be developed for this purpose and experiments in that direction are under way. Centrifuges of the imperforate-bowl type have also been tried, but it will be difficult to construct a machine of sufficient capacity to bring the cost of installation to a nonprohibitive amount. After the sludge has been reduced to a 50 per cent moisture content it can be readily and cheaply dried in the usual driers employed for drying organic ammoniates for fertilizers. As available space is an important consideration, an in-

vestigation into the possible depth of aerating tanks was made. Two pipes 14 in. in diameter were erected, one 36 ft. and the other 18 ft. high. The air, which was discharged through perforated pipes, was allowed to pass into each unit in equal amounts. The sewage used for this experiment came from the beef abattoir. Samples were taken at regular hours covering several days and the albuminoid, ammonia, nitrite and nitrate nitrogens, and the putrescibility were determined. As the results in either pipe were practically identical it was concluded that an aerating tank of any depth to 36 ft. will produce as good results as a more shallow tank in respect to purification of sewage. Economy in consumption of air should also be considered in this connection.

The bacteriological data are too meagre to warrant conclusions, but two facts are apparent: (1) three or four hours' aeration of the sludge from the settling chamber increases the number of organisms, but further aeration reduces them somewhat; (2) the organisms grow better at 20° C. than at 37° C. as might be expected. Throughout the records there seems to be a correlation between warm sewage temperatures about 75° F. and inactivity of the organisms, which results in an inactive sludge. This may be an obstacle that will prevent the placing of a disposal plant close to the abattoir where the sewage temperature may suddenly change from cold to hot or vice versa.

The results of the experimental work warrant the belief that this process offers more promising possibilities than any of the other methods of disposing of packing-house wastes hitherto proposed. The relatively small area required for installation, the comparatively high nitrogen content of the sludge, the comparative clarity and stability of the effluent, and the relatively short time of treatment are perhaps the most important features of the process.

Lime Sales in 1915.

The lime sold in the United States in 1915, according to G. F. Loughlin, of the United States Geological Survey, amounted to 3,589,679 short tons, valued at \$14,336,756, an increase of 6.2 per cent in quantity and 8 per cent in value over the figures for 1914. The average price per ton, \$3.99, was 7 cents more than that of 1914. The value of lime sold for chemical works, sugar factories, fertilizer, steel works, and miscellaneous purposes increased and more than offset decreases in the value of lime sold for building, paper mills, and tanneries. The number of plants in operation decreased from 954 in 1914 to 905 in 1915, and the number of kilns in active operation from 2,406 to 2,331.

Sales of hydrated lime continued to increase in 1915, amounting to 581,114 tons, valued at \$2,457,602, an increase of 12.8 per cent in quantity and 9.7 per cent in value over the sales in 1914. The average price per ton in 1915, however, dropped 12 cents, to \$4.23.

¹Am. Pub. Assoc., "Standard Methods for the Examination of Water and Sewage," 2nd Ed., 1912, 63.

THE BIHN-JONES AUTOMATIC BLOW CASE FOR LIFTING LIQUIDS BY MEANS OF COMPRESSED AIR.

It has long been the effort of inventors to obtain an automatic device which would turn on and off the valves necessary for the operation of lifting liquids by compressed air and a number of apparatus have from time to time appeared which have been claimed to accomplish the purpose.

One of the latest of these is the Bihn-Jones Automatic Air Device, which is very simple in construction and operation. Floats and other mechanism are omitted from within the blow-case or egg. The air device is placed directly on top of the blow-case

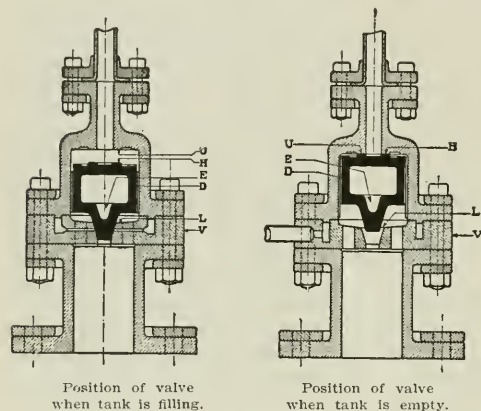


Fig. 1.

and can be installed in a very few moments without interrupting the process of manufacture.

The automatic blow-case complete consists of any suitable blow-case or acid egg, in the supply line of which is placed a check valve and in the air line of which is placed the Bihn-Jones Automatic Air Device, the latter being the chief feature and essential part of the entire system.

DETAILS OF THE AIR DEVICE.

The air device is composed of a base (V), see Fig. 1, which contains a seat (L) to which a number of ports for the admission of compressed air lead from an air chamber, which completely surround the seat.

A piston disc (D) having a conical seat (E) on its lower surface, which connects with the seat (L) in the base, thus completing the compressed air valve. There is also a flat circular exhaust valve seat (U) on the upper surface of this disc.

A hood is bolted to the base, thus forming a cover for the apparatus and a cylinder in which the piston-disc (D) moves. This hood contains an exhaust port which connects with a vent pipe. Around the exhaust port of the hood, there is formed a flat circular seat (H) which contacts with the seat (U) on the upper

surface of the piston-disc (D), and thus completes the exhaust air valve.

DETAILS OF OPERATION.

Liquid from a supply tank (A) flows by gravity through a check valve (C) into the blow-case (J)

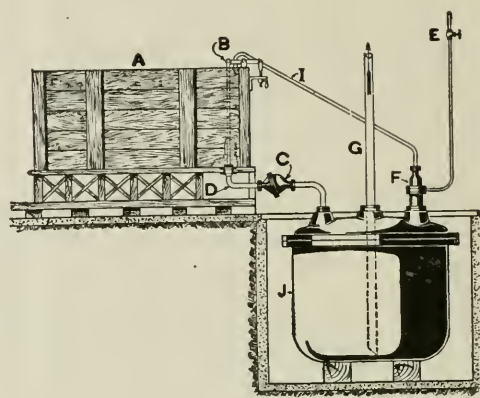


Fig. 2.

and rises until it reaches the base of the disc (D) of the Automatic Air Device (F), which it raises slightly, thus permitting compressed air to enter. The sudden release of the compressed air forces the disc (D) upward against its upper seat (U), thus closing the exhaust valve to the vent pipe (I).

The air thus prevented from escaping exerts its pressure on the top of the liquid, closes the check valve (C) and forces the liquid through discharge pipe (G) to its destination.

When the level of the liquid reaches the opening of the discharge pipe at the bottom of the blow-case, the compressed air follows the liquid out through the discharge line (completely clearing it of liquid), and escapes momentarily at the end of the discharge line. The expansion of the air, in the blow-case, due to the decreasing load as the liquid is forced out of the discharge line, causes a reduction in pressure in the blow-case sufficient to permit the disc of the air device to drop into its lower seat by its own weight. This simultaneously closes the ports of the compressed air valve and opens the exhaust air valve, thus releasing the exhaust air in the blow-case.

The check valve now opens due to the head of the liquid and the blow-case begins to fill, thus repeating the operation.

During the filling of the blow-case the exhaust air or gas which remains after pumping is displaced by the incoming liquid and escapes through surge holes in the base of the air device, passes through openings at the side of the disc and escapes through the exhaust port and the vent pipe (I).

In order to show the efficiency of operation of the Bihn-Jones apparatus, the acid eggs for a chamber set

about to be equipped with the Automatic Air Device, were tested for comparative air consumption and charts made and reproduced below show, graphically, the comparison in air used between the automatic and hand-operated blow-cases.

The blow-cases, seven in number, and of 5-ton capacity each, were operated by hand under the normal conditions of the plant. The chart, Fig. 3, shows the large and variable quantity of air used during the 24-

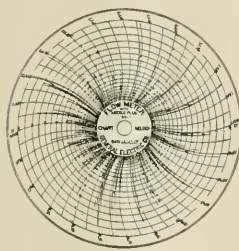


Fig. 3.

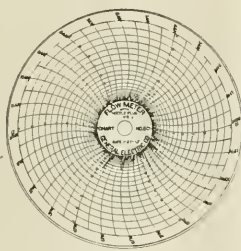


Fig. 4.

hour period of hand-operation, the heavy irregular lines indicating the exact travel of the needle and the comparative consumption of air.

Maintaining identical conditions throughout, but with Bihn-Jones Air Device installed on each blow-case, the chart, Fig. 4, was made. The difference is striking. The charts show very clearly and positively the comparative amounts of air used. In one case large irregular quantities, while in the other a small steady flow. This is conclusive evidence that the saving in compressed air and consequent reduction in size of compressor required is an item which cannot be ignored. The Bihn-Jones automatic air device described above is manufactured by Schutte & Koerting Co., 1252 N. 12th St., Philadelphia, Pa.

The Federal Trade Commission has completed its final report on the causes for the rise in gasoline prices and probably will send it to Congress in a few days. It is understood it will be more specific than the preliminary report sent to Congress several months ago, in which the Commission set forth facts discovered but made no deductions or recommendations for legislation. The final report, it was said, will go into detail as to an apparent lack of sufficient competition between companies producing gasoline. No recommendations for prosecution of any concerns are expected and none have been made to the Department of Justice. It is understood, however, that Congress will be told that the remedy for present conditions lies in some sort of regulation of gasoline manufacturers to insure real competition, or as a last resort in creation of Government machinery authorized to fix prices. Legislation by Congress would be necessary to effect either proposal.

BOOK REVIEWS

Ozone.—By A. Vosmaer, Ph. D. XII. 197 pages, illustrated. Published by D. Van Nostrand Co., New York; \$2.50 net.

In the volume Dr. Vosmaer gives the results of his investigations and experience with ozone, extending over a period of some 15 years. A feature of the book is the discussion on brush discharge. This is treated at considerable length and much light is thrown on the possibilities of this particular phenomenon. The book is divided into four parts: (1) Nature of ozone, (2) manufacture of ozone, (3) uses of ozone, and (4) list of American patents bearing on ozone, bibliography and index.

Identifications of Pure Organic Compounds.—By Samuel Parsons Mulliken, Ph. D., Associate Professor of Organic Chemical Research at Massachusetts Institute of Technology. IX. 327 pages. Published by John Wiley & Sons, Inc., New York; \$5 net.

This is Volume II of "A method for the identification of pure organic compounds by a systematic analytical procedure based on physical properties and chemical reactions." It contains classified descriptions of about 4,000 of the more important compounds of carbon with the elements nitrogen, hydrogen and oxygen, including the alkaloid and many drugs, proteolytic products, intermediates of the dyestuff industry, etc. In the preparation of this book the author has, in general, followed the system of ordinate, generic and specific tests initiated in Volume I. Certain improvements, however, have been made, the more important of these being a reduction in the number of genera in Order II as compared with Order I; an increase in the proportion of carefully verified specific characterizations; and a more convenient and flexible notation and arrangement for both specific characterizations and numbered tests.

The Metallography and Heat Treatment of Iron and Steel. By Albert Sauveur, Professor of Metallurgy and Metallography in Harvard University and the Massachusetts Institute of Technology. Published by Sauveur & Boylston, Metallurgical Engineers, Cambridge, Mass. 504 pages; \$6.

This is a fully revised and enlarged edition of Professor Sauveur's "Metallography of Iron and Steel," published in 1912. In view of the fact that a large portion of the book is devoted to the study of Heat Treatment, the new title appears to be more accurately descriptive of the contents. The edition contains 50 pages of new matter and nearly 100 new illustrations have been added. Practically every chapter has been revised to cover recent developments in the metallography of iron and steel and the applications of theoretical considerations to

industrial practice in the domain of heat treatment. The scope of the book is indicated by the following table of contents: I. Apparatus for the Metallographic Laboratory. II. Manipulations. III. Apparatus and Manipulations, continued. IV. Pure Metals. V. Pure Iron. VI. Wrought Iron. VII. Low Carbon Steel. VIII. Medium High and High Carbon Steel. IX. Impurities in Steel. X. The Thermal Critical Points of Iron and Steel. Their occurrence. XI. The Thermal Critical Points of Iron and Steel. Their causes. XII. The Thermal Critical Points of Iron and Steel. Their effects. XIII. Cast Steel. XIV. The Mechanical Treatment of Steel. XV. The Annealing of Steel. XVI. The Hardening of Steel. XVII. The Tempering of Hardened Steel. XVIII. Theories of the Hardening of Steel. XIX. The Cementation and Case Hardening of Steel. XX. Special Steels. General Considerations. XXI. Special Steels. Constitution, Properties, Treatment and Uses of Most Important Types. XXII. Cast Iron. XXIII. Impurities in Cast Iron. XXIV. Malleable Cast Iron. XXV. Constitution of Metallic Alloys. XXVI. Equilibrium Diagram of Iron-Carbon Alloys. XXVII. The Phase Rule. Appendix. Nomenclature of the Microscopic Constituents.

American Fertilizer Hand Book.—400 pages. Published by Ware Bros. Co., Philadelphia, Pa. \$1.

The present volume is the 9th annual edition (1916) of the American Fertilizer Hand Book. It contains special articles and statistics—of interest to the fertilizer trade. Directory of the fertilizer manufacturers of the United States—keyed to indicate the exact nature of their business and arranged by States. Classified directory of the allied fertilizer trades—which includes manufacturers of fertilizer machinery and factory equipment; manufacturers of and dealers in fertilizer materials and supplies; brokers, importers and exporters, chemists; phosphate miners; sulphuric acid plants; lead burners, etc., etc. Directory of the cottonseed oil mills—arranged by states. Directory of packers and renderers—arranged by states and keyed to indicate meat packing houses, rendering plants and manufacturers of fertilizer materials.

Lignite as a fuel in an electric station has given highly economical results according to Engineering. At the Weiswiler station, near Acken, Germany, lignite of about 2,700 B.t.u. per pound, and with 64 per cent moisture, is burned directly on the boiler grates. About 4 kg. or 8.8 lb. of lignite are used per kilowatt-hour generated. Ten tons of lignite is valued at 10.85 marks so that the fuel cost on this basis works out at about 0.1 cent per kilowatt-hour. Other charges amount to 0.135 cent per kilowatt-hour, making the cost of electric energy roughly 0.2 cent per kilowatt-hour.

THE WATER CONSUMED IN PAPER MANUFACTURE.*

In American fine paper mills, where linens, bonds and ledgers are made from rag stock, the consumption of water is estimated to amount to at least 1,000 gallons for every pound of dry paper produced. The general subject of water consumption and fiber recovery from waste waters of the paper and pulp industry has been treated in an article appearing in the *Wochenblatt für Papierfabrikation* for Feb. 20, 1916, copies of which have been circulated among the members of the News-Print Manufacturers' Association by Secretary Steele. It is there noted that reliable data in regard to the water requirements and amount of waste water in paper mills are rare.

In an early contribution by Prof. E. Kirchner he put the requirements of water for wood-grinding plants and white paper mills at 48 to 120 gallons for each pound of dry product, with approximately as much waste water. Later Superintendent Wieselgren (*Wochenblatt*, 1909, page 504) made the following report of water consumption on a rag paper mill operating two machines:

	Gallons.
Halfstuff	103.51
Bleaching	69.02
Wholesale	8.62
Paper machine	69.02
Size cooking and washing	8.62
Total	258.79

The water consumption in this plant necessitated a supply of 1,981.27 gallons of water a minute. For a newsprint machine the water consumption was estimated to represent 47 gallons to the pound.

The remainder of the article is interesting as showing the thoroughness and minute care with which German papermakers take up all problems relating to the industry, statistics being given of the water consumption and loss of fiber in various mills, as well as points on economies to be effected by the use of save-alls in the recovery of fiber from waste waters. The figures for water consumption appear exceedingly low as compared with calculations made in American plants. A Swedish authority is quoted on the water consumed in Swedish mills in the production of one pound of dry pulp and paper, respectively. The number of gallons of water consumed is stated as follows: Wood-grinding plants, 42; sulphate mills, 30; sulphite mills, 36; paper machines, 27.

Losses of fiber are calculated by the Swedish authority referred to (Tor Carlson: *Wochenblatt für Papierfabrikation*, 1910, page 551) as follows: Wood-grinding plants, 5 to 6 per cent of the quantity produced; sulphate mills, 2.2 per cent; sulphite (unbleached) mills, 2 to 3 per cent; sulphite (bleached), 4 per cent; newsprint, 11.3 to 14.8 per cent; sulphite paper, 3.7 to 6.4 per cent; rag paper, 2 per cent.

Concerning present conditions in modern German

*From Paper.

mills, the author of the article in the *W'ochenblatt* makes the following observations:

Important economical advantages are to be gained by following the plan of allowing the paper machine manufacturing water to make as a rule but one circulation in the manufacturing process and of only discharging the waste water from the establishment after all oil, grease and impurities, light in themselves, have been removed and the greater portion of the paper stuff in the waste water is collected by sedimentation and used over again in the manufacture of pulp or paper. Considerable saving of fresh water and recovery of important quantities of fibers that formerly went to waste, and as a consequence, a material saving of money, are the readily evident results.

I may remark that as it happened, I only handled the O. Schmidt savealls, German patent No. 191,325. I myself doubted whether the statement of one of the foremost German fine and print paper mills, that these savealls from the waste water from papers made without wood, were capable of recovering 97 per cent of the fibers they contained, was correct. It was however stated that the tests had been personally very conscientiously conducted on many occasions.

In a large high power grinding plant, which a few years ago produced 13,228 tons of dry pressed wood-pulp in twenty-four hours, only 211,336 gallons of fresh water a minute was used and just as much waste water run into the sewer. There was therefore required, for 1 pound of mechanical pulp, only $211,336 \times 24 \times 60 \div 13,228 = 11,503$ gallons of fresh

2000

water.

The waste water, on entering the Schmidt saveall, contained .051 oz. per gallon, and on leaving it contained .010 oz. per gallon, showing a fiber recovery of 81 per cent. The saveall consequently recovered 2.95 per cent of the entire production. It contained therefore daily $.0295 \times 13,228 = .390$ tons, and per year (reckoning 320 days), 124.8 tons. This means returning a profit of \$2,618 to \$2,856 and relieving the river or stream receiving the waste water of the unsightly and possibly objectionable fiber residue.

In the case of waste water carrying only small quantities of pulp as in woodgrinding establishments, a recovery of 81 per cent is certainly favorable as compared with the Carlson figures for water consumption and fiber losses.

The newsprint machine waste waters that have been passed through Schmidt savealls for the purpose of freeing them from fiber, differ considerably from the grinding plant waters, in containing large quantities of clay. If I calculate averages from the many to 492 feet per minute speed, approximately 17,974 gallons of water per pound of paper must be allowed, experiments made, I find, that at the ordinary 393½ which, on an average, allows for the recovery of .134 oz. per

gallon of stuff, that is to say, 4.8 ozs. of stuff to a pound of paper. In other words, 30 per cent recovered substance amount to 95 per cent or more of recovered in part in a dirty condition, is now saved. I have also found that these .134 oz. per gallon of recovered substance amount to 95 per cent or more of all the stuff that loads the paper machine waste water, which in place of being lost as formerly, now only makes a circulation; in the course of a year this represents a large saving. If we calculate 13,779 tons as the daily production of a machine, the saveall returns daily 4.134 tons of good stuff into circulation; that is, in a year of 300 working days, 1,240 tons less of wholestuff has to be used, a volume of wholestuff that represents a value of at least \$33,320.

If we attempt the recovery of the stuff by any other method we shall find that as regards cleanliness and quantity, we cannot obtain anything like the results here set forth. The smaller proportion of impure pulp will be obtained at the expense of much hand labor and use of power. We shall also have to take into account various troubles and injurious influences on the paper machine, due to impure pulp. The automatic return of pure pulp fiber by circulation into the paper machine is accompanied by other conspicuous advantages.

The clean pulp, obtained by sedimentation in the saveall and returned directly to the paper machine consists of sized, very fine fibers and particles of clay, which impart to the paper in course of production particularly good properties. As the greater portion of the sizing material, fibers and clay that pass through the wire is not lost, the machine wire may be made stronger (in place of No. 80 about No. 70) bringing the advantage of longer endurance for the wire of a higher rate of speed for the machine. A by no means unimportant gain for the production is obtained by the greater purity of the pulp carried directly from the filter mentioned on to the paper machine, the wire and felts remaining clean longer, consequently requiring less frequent washing and therefore lasting longer. There are not as many stoppages and less waste is made.

Carlson's loss of fiber, in print paper manufacturing, is given as 11.3 to 14.8 per cent; if this applies only to fibers, it would then agree with my investigations, for in the .134 oz. per gallon quoted by me above, about half of this is clay.

The ninth annual meeting of the American Institute of Chemical Engineers will be held in New York City, Jan. 10-13, 1917.

The annual statement on silica in 1915 is now available for distribution by the Geological Survey. During the year the production of silica in various forms amounted to 243,340 short tons, valued at \$1,270,835.

PRICES OF CHEMICALS, OILS, ETC., AUGUST, 1916

WHOLESALE PRICES PREVAILING IN NEW YORK MARKET ON AUGUST 12

CHEMICALS, INORGANIC.

Acetate of lime, 100 lbs.....	\$ 7.25	@ 7.75
Alum, ammonia, crystals, lb.....	.16	@ .24
Aluminum sulphate, 100 lbs.....	.04	@ .04½
Arsenic, white, lb.....	.06½@	.06½
Barium chloride, ton.....	110.00	@ 115.00
Barium nitrate, kegs, lb.....	.14	@ .16
Bleaching powder, drums, 100 lbs.....	5.00	@ 6.00
Blue vitriol, car lots, 100 lbs.....	9.50	@ 10.00
Blue vitriol, powdered, 100 lbs.....	14.00	@ 16.00
Borax, car lots, f. o. b. N. Y., 100 lbs....	7.50	@ 8.00
Brimstone, crude, ton.....	35.00	@
Caustic soda, 74 to 76%, lb.....	.04	@ .04½
Chalk, precipitated, cases, lb.....	.05½@	.06½
Glauber's salt, bags, 100 lbs.....	.60	@ .70
Nitric acid, 36 to 42°, 100 lbs.....	7.50	@ 8.00
Phosphoric acid, 1.750 lb.....	.30	@ .34½
Potassium bichromate, lb.....	.40	@ .41
Potassium carbonate, calcined, 90 to 96%, lb.....	.90	@ 1.00
Potassium chlorate, crystals, lb.....	.46	@ .52
Potassium cyanide, bulk, 100 lbs.....	.45	@ .50
Quicksilver, flasks.....	75.00	@ 76.00
Silver nitrate, ounce.....	.41½@	.41¾
Soda ash, 48%, 100 lbs.....	2.75	@ 3.00
Sodium acetate, lb.....	.14	@ .15
Sodium bicarbonate, American, 100 lbs....	1.65	@ 2.00
Sodium bichromate, lb.....	.30	@ .31
Sodium chlorate, 100 lbs.....	.30	@ .35
Sodium hyposulphite, in bbls., 100 lbs.....	2.00	@ 2.25
Sodium nitrite, lb.....	.12	@ .14
Sodium sulphide, crystals, 100 lbs.....	3.75	@
Sulphuric acid, 60° and up, cwt.....	1.50	@ 2.00
Sulphuric acid, 66°, ton.....	30.00	@ 35.00
Talc, domestic, spot, ton.....	15.40	@
Tin bichloride, 50°, 100 lbs.....	13.50	@
Tin oxide, lb.....	.43	@ .45
Zinc oxide, lb.....	.11	@ .15

CHEMICALS, ORGANIC.

Acetanilid, lb.....	.65	@ .75
Acetic acid, 28%, 100 lbs.....	5.50	@ 5.75
Acetic acid, glacial, 99½% carboys, lb.....	.45	@ .50
Acetone, drums, lb.....		@
Alcohol, denatured, 188 proof, gal.....	.55	@ .56
Alcohol, grain, 188 proof, gal.....	2.68	@ 2.70
Alcohol, wood, 95%, gal.....	.65	@
Amyl acetate, gal.....	5.00	@ 5.50
Benzoic acid, from tuluol, cwt.....	7.75	@ 8.00
Carbolic acid, drums, crystals, lb.....	.60	@ .70
Carbon, tetrachloride, lb.....	.17	@ .20
Chloroform, lb.....	.50	@ .55
Citric acid, domestic, crystals, lb.....	.67	@ .67½
Cresole, U. S. P., gal.....	1.36	@ 1.90
Ether, U. S. P., 1900, lb.....	.15	@ .20
Formaldehyde, 40%, carboys, lb.....	.11½@	.12
Glycerine, dynamite, lb.....	.35½@	
Pyrogalllic acid, crystal, lb.....	2.90	@ 3.20
Salicylic acid, lb.....	2.25	@
Tannic acid, technical, lb.....	.60	@
Tartaric acid, crystals, U. S. P., lb.....	.66	@ .66½

DYE MATERIALS.

Acid orange, lb.....	1.75	@ 2.20
Aniline oil, drums, imported, lb.....		@
Aniline, domestic, lb.....	.31½@	.37½
Benzol (white), gal.....	.70	@ .80
Bismarck brown, lb.....	2.25	@ 2.85
Carmine, lb.....	5.00	@ 5.10

Cochineal, silver, lb.....	.75	@ .80
Cochineal, black, lb.....	.73	@ .75
Gambier, lb.....	.10	@ .10½
Indigo, madras, lb.....	1.50	@ 1.50
Logwood extract, 51°, lb.....	.25	@ .28
Madder, Dutch, lb.....	.28	@ .30
Methyl, violet, lb.....	9.00	@ 15.00
Methylene, technical, lb.....	7.00	@ 10.00
Prussian blue, soluble, lb.....	1.75	@ 2.00
Sulphur, black, lb.....	.90	@ 1.90
Sulphur, brown, lb.....	.30	@ .60
Zinc dust, prime to heavy, lb.....	.25	@ .30
Zinc oxide, American, lb.....	.11	@
Zinc sulphate, lb.....	.07½@	.09

ESSENTIAL OILS.

Almonds, bitter, lb.....	12.50	@ 14.00
Amber, crude, lb.....	12.50	@ 14.00
Anise, technical, lb.....	1.05	@ 1.10
Camphor, Japanese, 72 lb. cans, lb.....	.16	@ .20
Cinnamon, lb.....	19.00	@ 20.00
Clove, lb.....	1.20	@ 1.25
Cubeb, lb.....	3.25	@
Ginger, lb.....	5.50	@ 6.50
Limes, distilled, lb.....	2.75	@ 3.00
Pennyroyal, prime, American, lb.....	1.65	@ 1.85
Peppermint, prime, American, lb.....	1.80	@ 1.90
Spearmint, oz.....	1.60	@ 1.75
Wintergreen, synthetic, oz.....	2.25	@ 2.55
Wormwood, oz.....	2.25	@ 2.60

FERTILIZER MATERIALS.

Ammonium sulphate, 100 lbs.....	3.55	@
Blood, dried, N. Y., 100 lbs.....	2.95	@
Blood, dried, f. o. b. Chicago, 100 lbs.....	2.65	@
Bone black, sugar discard, ton.....	.27	@ .30
Bone, oil discard, ton.....	.18	@ .20
Muriate of potash, 80-85%, ton.....	400.00	@
Phosphate, acid, per unit, ton.....	80.00	@ 90.00
Sulphate of potash, 90%, ton.....	275.00	@
Tankage, Chicago, 100 lbs.....	2.50	@

OILS.

Castor oil, No. 3 bbls., lb.....	.13½@	
Corn oil, crude, 100 lbs.....	7.75	@ 7.85
Corn oil, refined, 100 lbs.....	8.91	@ 8.96
Cylinder oil, light filtered, gal.....	.20	@ .25
Cylinder oil, dark filtered, gal.....	.19	@ .20
Fusel oil, refined, gal.....	6.00	@ 6.25
Linseed oil, carlots, gal.....	.72	@
Menhaden oil, crude, Southern, gal.....	.48	@ .49
Naphtha, auto, 68@72°, gal.....	.37¼@	.36¾
Paraffine oil, high viscosity, gal.....	.25½@	.26½
Soya oil in bbls., lb.....	.07¼@	.08
Spindle oil, No. 1, gal.....	.19	@ .20
Spindle oil, 20 gravity, gal.....	.17	@ .18
Tar oil, commercial, gal.....	.25	@ .27
Turpentine, gal.....	.45	@ .46

WAXES, ETC.

Beeswax, ordinary, pure, lb.....	.32	@ .36
Ceresin wax, yellow, lb.....	.10	@ .30
Ceresin wax, white, lb.....	.14	@ .40
Japan wax, lb.....	.14	@ .14½
Paraffine, crude, 124-126 mp., lb.....	.05¼@	.05¾
Pitch, pine, first grade, bbl.....	4.50	@
Rosin, B grade, N. Y., bbl.....	6.75	@
Stearic acid, lb.....	.11	@ .13½
Tar, retort, bbl.....	7.00	@ 7.50

NOTES OF CHEMICAL AND ALLIED INDUSTRIES., AUGUST, 1916

Air Products.—The Linde Air Products Co., of which G. H. Watson, 155 Chandler St., Binghamton, N. Y., is general manager, will erect two factory buildings at Binghamton at a cost of about \$40,000. H. D. Edwards, 42d St. Bldg., New York City, is the engineer.

Alcohol.—The Pennsylvania Product Co. will erect a factory at Christiansa, Pa., for the manufacture of denatured alcohol. It will have an initial capacity of 4,000 gals. daily, and will require an expenditure of \$20,000 for buildings and \$22,000 for machinery.

Alcohol.—The Canton Corn Products Co. of Baltimore, Md., has been incorporated with a capital stock of \$250,000, and will engage in the manufacture of alcohol. Dan Cloud, 437 Title Bldg., Baltimore, is one of the incorporators.

Alloy.—The Electro Metallurgical Co. has awarded a contract for the erection of a 60x70-ft. reinforced concrete and brick building at Highlandtown, a suburb of Baltimore, for use as a plant for turning out alloy. Konstantin Jouvceff is president of the company.

Beet Sugar.—The Great Western Sugar Co. contemplates the erection of a beet sugar plant at Missoula, Mont.

Beet Sugar.—The Pingree Sugar Co., incorporated late in July with a capital stock of \$1,000,000, will take over the ownership and management of the old Corcoran beet sugar plant at Corcoran, Cal. R. R. Nickerson, president of the San Joaquin Valley Sugar Co., one of the incorporators, and James Pingree of Ogden have purchased the Corcoran plant, which was built at a cost of \$1,000,000, and has been shut down for some time. The plant is to be improved and opened next year. It has a capacity of 800 tons of sugar beets a day.

Beet Sugar.—The Montana-Utah Sugar Co. has filed its articles at Salt Lake City, Utah. The company has a capital stock of \$100,000, and proposes the construction of a plant next year in the Bitter Root Country in Montana. O. C. Beebe and George E. Sanders of Salt Lake City are interested. They also were organizers of the Oregon-Utah Sugar Co.

Beet Sugar.—The Dyer Construction Co., Cleveland, O., has been awarded a contract for the construction of a \$500,000 sugar factory to be located about 5 miles from Smithfield, Utah. The West Caches Sugar Co. also is understood to be planning to erect a 500-ton factory to cost \$500,000, near Smithfield. This latter company is owned by some 50 farmers of Northern Utah, among these being B. Y. Benson, Trenton; George Y. Smith of Smithfield, and G. G. Wright of Salt Lake City.

Carbolic Acid.—The Allen Chemical Co. of Allentown, Pa., has been chartered with a capital stock of

\$50,000. The company will manufacture carbolic acid and also will produce other chemicals, particularly pharmaceutical preparations. Dr. I. F. Huebner, James K. Bowen and William H. Gangwere are the incorporators.

Cement.—The Thos. Millen Cement Co. has awarded a contract to W. J. Burns Co., 420 Bastable Bldg., Syracuse, N. Y., for rebuilding the cement plant at Jamesville, N. Y., which was recently destroyed by fire.

Cement.—The Black Construction Co., Alaska Bldg., Seattle, Wash., has been awarded the general contract for the construction of a 2,200-bbl. cement plant at Darrington, Wash., for Galbraith, Bacon & Co., of Seattle. The plant will be located on a 600-acre tract of land and will call for an expenditure of about \$1,000,000. H. Bittman, Securities Bldg., Seattle, Wash., is the engineer.

Cement.—The Three Forks Cement Co., Trident, Mont., has purchased the plant of the Hanover Gypsum Co., Hanover, Mont. It is reported new owners plan to construct a 2,500-bbl. cement plant calling for an expenditure of \$1,000,000. The stockholders of the Three Forks Co. also control the Oregon Portland Cement Co., Portland, Ore., which recently opened a large cement plant at Oswego, Ore.

Chemical.—The Shepherd Chemical Co. of Cincinnati, O., has been organized with a capital stock of \$10,000, and will construct a plant.

Chemicals.—Montgomery Chemical Works, 213 Courtland St., Baltimore, Md., proposes erection of addition to its plant at Curtis Bay, Md.

Chemicals.—March & Co., Rahway, N. J., have awarded a contract for a \$25,000 addition to their chemical plant at Rahway. Salmond Bros. Co., Arlington, N. J., is the contractor, and W. F. Bower, 44 Harrison St., East Orange, N. J., is the architect.

Chemicals.—The Wm. R. Warner Co., 639 North Broad St., Philadelphia, Pa., will expend about \$300,000 for the erection of a factory. Wm. Steele & Sons, 1600 Arch St., Philadelphia, are the engineers.

Chemicals.—The Hoistman Chemical Co. proposes construction of an addition to its plant at Redwood City, Cal.

Chemicals.—The Monsanto Chemical Works of St. Louis, Mo., of which John F. Queeny is president and Louis Veillon, vice president, have awarded the contract to the Gilsontite Construction Co., St. Louis, for the erection of two factory buildings to cost about \$90,000. Brenneke & Fay, Fullerton Bldg., St. Louis, are the engineers.

Chemical Laboratory.—Bids closed early this month for the construction of a chemical laboratory at Wilmington, Del., for Francis I. Du Pont. The structure is to be 2 stories, 35x40, 22x233 and 22x

100 ft., and is to cost \$35,000. R. L. Perrot, 34 S. 17th St., Philadelphia, is the architect.

Cotton Seed Oil.—Texas Refineries Co., San Antonio, Tex., proposes expending about \$250,000 for improvements to its plant. These will include eight cotton seed oil presses, refining equipment, conveyor system, 750 h.p. engine and three new boilers.

Dyes.—The Butler Chemical Co. will begin operating its dye plant at Butler, N. J., about Sept. 1. The company already has one plant in East Bloomingdale, N. J., and another at Smiths Mills.

Dyes.—The Reading Chemical Co. of Reading, Pa., whose dye department was destroyed recently by fire, with a loss of \$30,000, has work underway on a temporary factory, which will be ready for operation by Sept. 1.

Dyes.—The Indiana Creek Fertilizer Works at Byrdton, Va., has been purchased by the J. Y. J. Corporation, 59 Fulton St., New York, and will be converted into a dye factory for which the machinery has been ordered. J. T. Richards is the superintendent.

Dyes.—The Gulf Reduction Co., of Pensacola, Fla., has plans under contemplation for increasing its daily capacity from $\frac{1}{2}$ ton to 5 tons.

Dynamite.—The General Explosives Co., incorporated recently with a capital stock of \$50,000, proposes the establishment of a plant at Joplin, Mo., for the manufacture of dynamite. The company has offices at 2036 Railway Exchange Bldg., St. Louis, Mo. The officers are as follows: E. Wm. Hawley, St. Louis, is president; W. W. Edwards, New York, vice president; Albert J. Rawlings, Chicago, Ill., secretary.

Explosives.—The General Explosives Co., St. Louis, Mo., has been incorporated with a capital stock of \$50,000, to be increased later, and will manufacture explosives and shells. The stockholders are E. William Hawley, Railway Exchange Building, St. Louis; Walter W. Edwards and Joseph M. Owne, of Chicago, and Alfred J. Rawlings, New York.

Fertilizer.—The Florida Reduction Co. of Miami, Fla., has been organized by New York capitalists, and proposes the installation of a \$60,000 experimental plant for the production of fertilizer from sponges. W. H. Vreeland is president, and J. B. Dill, manager. L. C. Haughey, Miami, Fla., is vice president.

Fertilizer.—The Terre Haute Hide & Fertilizer Co., Terre Haute, Ind., will erect a \$7,000 fertilizer plant in Lost Creek Township.

Fertilizer, Potash.—The Mifflin Chemical Corp., recently incorporated at \$100,000, has started operations in its plant at Delaware Ave. and Mifflin St., Philadelphia, Pa. This concern is making foundry molasses, fertilizers, materials for printers' inks, and is about to engage in the recovery of liquid potash. The company was incorporated by Philip

Publicker, David Berg, Leo G. Bernheimer, Joseph H. Sundheim and I. L. Lipschutz, all of Philadelphia.

Graphite.—The Southern Star Graphite Co., of Louisville, Ky., a \$50,000 corporation, proposes the establishment of a 400-ton mill at Ashland, Ala., for the recovery of graphite. George G. Montz, Louisville, is an incorporator.

Gypsum.—The U. S. Gypsum Co. is reported contemplating the erection of a large plant near Rapid City, S. Dak.

Magnesite.—The Joshua Hendy Iron Works, Porterville, Cal., has purchased the plant and equipment of the California Magnesite Co., Porterville, Cal. It is reported the plant will be completed according to the original plans to handle crude magnesite on a custom basis.

Metals.—The U. S. Metal Refining Co., Roosevelt, N. J., has awarded a contract for the construction of a 2-story, 50x115-ft. laboratory building.

Nickel.—The British American Nickel Co., and the International Nickel Co. of Canada, Ltd., will take immediate steps for the erection of nickel refining plants in the Province of Ontario, Canada. The first mentioned company is about to commence work for the development of power on the Wana-pitel River near Sudbury, Ont., for its smelter and will erect a refinery at the same time. The International Nickel Co., the Canadian branch of the United States company, was incorporated the latter part of July with a capital stock of \$5,000,000, and head offices at Toronto.

Nitrate.—Nonnabo Chemical Co., East Providence, R. I., is erecting a 2-story, 65x240-ft. nitrating building to cost about \$25,000. Richard Le Bowen is general manager.

Paint.—The Ottawa Paint Works, Ltd., Ottawa, Ont., has been incorporated with a capital stock of \$250,000, and will engage in the manufacture of paints, varnishes, etc. The incorporators include Thomas C. Hickman and George D. Kelley.

Paint.—The H. B. Davis Co., 407 Keyser Bldg., Baltimore, Md., will erect four additional units to its plant at Keyser and Bayard Sts., Baltimore. These will consist of reducing house 24x48 ft., a gun house 24x48 ft., tank 28x50 ft., and oil house and furnace 22x48 ft. The buildings will be of brick and reinforced concrete construction. C. W. Stubbs, Equitable Bldg., Baltimore, is the contractor. J. E. Moxley, Jr., 531 N. Calhoun St., Baltimore, is the architect.

Paint.—The Lancaster Fire Proofing & Paint Co., Jobbers, Lancaster, Pa.; the Schroeder Paint Co., Manufacturers, and the Gould Selling Agency, of Ohio, Indiana and Michigan, have consolidated under the name of Lancaster Fire Proofing & Paint Co., Lancaster, Pa. The capital stock has been increased to \$150,000. S. M. Boyd is manager and treasurer.

Paper.—The International Paper Co., New York City, is understood to be planning to establish a plant in Canada.

Paper.—The following Canadian manufacturers have work underway or in contemplation for increasing the capacity of their paper plants: Union Bag & Paper Co., Three Rivers, Que., 100 tons daily capacity news print mill; Donnacona Paper Co., Donnacona, Que., an increase of 50 tons per day; Laurentide Paper Co., 200 to 400 tons a day; Ontario Paper Co., Thorold, Ont., additions and new machinery; Abitibi Power & Paper Co., Ltd., Iroquois Falls, Ont., to purchase two 235-in. paper machines; Price Bros. & Co., Ltd., Kenogami, Que., an addition to cost \$500,000; International Paper Co., 30 Broad St., New York, a 200-ton news-print mill in Canada.

Paper.—The Chester Paper Co., a subsidiary of the Scott Paper Co., of Philadelphia, has purchased a large lot of land on the west side of its plant at Chester, Pa., which will be used for improving and enlarging the manufactory, at a cost of \$250,000. Buildings to be used for the engine room, boiler house and factory purposes will be erected immediately. The old boiler house and engine room in the rear of the main building of the paper plant will be razed so that the main structure can be extended back to Front St. The improvements to plant will increase its capacity 50 per cent. A paper machine weighing 400 tons will be installed, the heater house will be enlarged from a capacity of 20 tons of pulp to 55 tons daily and a new bulkhead will be constructed in front of the property. A concrete-and-steel warehouse will be built, and also a special building for the paper machine. Officials of the company hope to have the new plant in operation by Oct. 1.

Paper.—The John Strange Paper Co. of Menasha, Wis., has plans well advanced for a new plant to be erected at Oshkosh, Wis., that will require an expenditure of nearly \$500,000. It is stated the new installation will manufacture paper boxboards, thus increasing the present capacity from 40 tons to 150 tons a day. The machinery contract is understood to have been placed.

Pigments.—The Chemical Pigments Co., St. Helena, Md., proposes erection of a 100x300 ft. plant.

Pigments.—E. J. Baton Co., Philadelphia, Pa., has been awarded the contract for the construction of a 1-story 300x100 ft. brick and concrete building at St. Helena, Md., to be used by the Chemical Pigment Corp., for the manufacture of chemical pigments. This company was incorporated last June with a capital stock of \$265,000. F. R. Hansell, of the Philadelphia Vinegar Co., 153 S. Front St., Philadelphia, Pa., being one of the incorporators. F. S. Havens, 1237 S. 57th St., Philadelphia, Pa., is the chemical engineer.

Potash.—John H. Sullivan of Pittsburgh, Pa., secretary of the Florence Mining Co., which is developing a number of alunite fields in Plute and Sevier Counties, Utah, has closed contracts for the erection of a plant and a branch railroad at Marysville, Utah, for the manufacture and transportation of potash. Engineers of the company, which is financed largely by Pittsburgh capital, have made reports warranting the expenditure of \$1,500,000.

Potash.—At the present time six concerns are actively engaged in the production of potash from kelp on the southern coast of California. Three companies are said to have made an aggregate investment of over \$3,000,000 in barges and special harvesting and reduction machinery.

Potash.—A Chicago syndicate of capitalists represented by T. Willoughby Cole have engineers in the field investigating potash deposit in Malheur and Haney Counties, Oregon. The syndicate proposes the improvement of 648,000 acres of land by irrigation and drainage, and the development of potash fields.

Potassium.—The Potassium Manufacturing Co., incorporated recently with a capital stock of \$250,000, proposes the construction of a kelp reduction plant at Long Beach, Cal., for the production of potassium products. J. I. Armstrong, Los Angeles, Cal., is the president.

Pulp and Paper Plants.—The Manitoba Power, Pulp & Paper Co. contemplates expenditure of \$2,000,000 for paper and pulp plants. These probably will not be erected until next year. A saw mill, however, will be built this year at Grand Rapids, Man.

Rubber.—The Agricultural Products Corp., a subsidiary of the International Rubber Co., 225 Fifth Ave., New York, proposes a factory at Tucson, Ariz., for extracting crude rubber from the wild guayule shrub. The company plans to also devote about 10,000 acres of land in that vicinity to growing the shrubs. Gen. L. H. Manning, Tucson, Ariz., is interested.

Rubber Goods.—Goodyear Tire & Rubber Co., 152 Simcoe St., Toronto, Ont., have awarded a contract to the Dominion Construction Co., 14 Wellington St. East, Toronto, for the erection of a \$750,000 factory at East Toronto.

Salicylic Acid.—The Bristol Chemical Works, organized recently, will engage in the manufacture of salicylic acid with plant at Bristol, Va. J. T. Ray, Damascus, Va., is president and manager.

Silk.—The Leon-Ferenbach Co., New York City, will organize a branch company and erect a 200x50-ft. silk mill at Johnson City, Tenn.

Silk.—Lewis Roessel Co. opened bids Aug. 10 for construction of an addition to its silk mill at Hazleton, Pa. The new buildings will be 4-story, and 2-story, 54x200 ft. and 27x70 ft. W. E. S. Dyer, Philadelphia, Pa., is the architect. Wm. Binney,

4th and McKinney Ave., Hazleton, is the local manager.

Silk.—Frank J. Miller, Architect, Peoples' Bank Bldg., Scranton, Pa., is preparing plans for a silk mill calling for an expenditure of about \$50,000.

Silk.—The De Grado Silk Finishing & Dyeing Co., Paterson, N. J., has awarded a contract to Elia & Martins, 436 Broadway, Paterson, for the erection of a \$30,000 silk finishing and dye mill.

Silk.—McBride Bros. have awarded contract to George H. Hardner, Allentown, Pa., for the erection of a \$35,000 addition to their silk mill at Fullerton, Pa. The new building will be 2-story and basement, 72x172 ft. There also will be a 1-story power house 30x145 ft. Ruhe & Lange, 10 N. 6th St., Allentown, Pa., are the architects.

Soda Ash.—The Ohio Valley Alkali Co., recently incorporated with a capital stock of \$350,000, proposes the erection of a \$200,000 plant for the manufacture of soda ash for use in glass making. This company is a subsidiary of the Glass Brick Co., which is now erecting a large plant. The incorporators include H. E. Marble, Cincinnati, O., and P. Barton, Norwood, O.

Sugar.—The Federated Sugar Manufacturing Co., incorporated recently, proposes the establishment of a sugar plant near Lombay, Fla. A. L. York, 4416 St. John Ave., Kansas City, Mo., is president.

Sugar.—The Haytian American Corp. has formed for the purpose of controlling public utilities and railroads at Port-au-Prince, Hayti, and the valleys adjacent to the capital, and to develop the sugar industry of these valleys. The new company is being financed by Breed, Elliott & Harrison, of Cincinnati, together with P. W. Chapman & Co., of Chicago. The company is to acquire existing public utilities, consisting of a wharf, railroad, electric power plant and tramway, at Port-au-Prince and to establish a centrale for the grinding of sugar cane to be produced on lands owned or controlled in the adjacent valleys. The company is to be capitalized at \$6,000,000 7 per cent preferred stock, \$12,000,000 7 per cent noncumulative participating common stock and 60,000 shares of founders' stock of no stated par value. It is expected to offer the stock in the market within the month or so. The directorate of the new company will include George B. Caldwell, New York City; P. W. Chapman, Chicago; F. A. Dillingham, New York; C. Edgar Elliott, Chicago; Philip W. Henry, New York City; S. Mallett Prevost, New York; E. Pavenstedt, New York; H. C. Staude, Hayti; George Turnure, New York; H. R. Tippenhauer, New York.

Sulphite Mill.—The Ontario Paper Co., Thorold, Ont., has awarded the contract to W. J. Trimble for the erection of a large sulphite mill.

Sulphite Plant.—The Rhinelander Paper Co., of which John Van Alstyne, Rhinelander, Wis., is

general superintendent, proposes building a sulphite plant and tower.

Tanlac.—The Carolina Tanlac Co. of Charlotte, N. C., has been incorporated with a capital stock of \$155,000. C. E. Hobbs, H. L. Taylor and G. M. Hubbard are incorporators.

Tannery.—The International Shoe Co., St. Louis, Mo., will erect a \$400,000 tannery building at Wood River, Ill. The contract for this work has been let to James Black Construction Co., Wright Bldg., St. Louis, Mo. Link, Wilbur & Trueblood, Carlton Bldg., St. Louis, Mo., are the architects. Oscar Johnson, 1505 Washington Ave., St. Louis, is president of the shoe company.

Zinc.—The American Zinc, Lead & Smelting Co., Granby, Mo., will erect a concentrating plant and install other machinery for 300 tons capacity each shift.

New Chemical Concerns Incorporated Since January 1, 1915.

Since January 1, 1915, new chemical and dye companies with an aggregate capital stock of nearly \$125,000,000 have been incorporated. This figure covers only corporations of over \$50,000 capitalization. Of the total \$65,565,000 is for concerns taking out incorporation papers during 1915 and \$59,628,000 is for the first seven months of the present year. The following figures, compiled by the New York Journal of Commerce, show the incorporations by months:

1915—	1915—
January\$1,630,000	July\$ 4,950,000
February 750,000	August 3,260,000
March 1,925,000	September 800,000
April 1,400,000	October 25,525,000
May 5,100,000	November 1,650,000
June 8,450,000	December 10,125,000
Total\$65,565,000	
1916—	1916—
January\$ 9,525,000	May\$ 6,800,000
February 37,945,000	June 553,000
March 1,450,000	July 330,000
April 2,575,000	
Total\$59,178,000	
Grand total\$124,743,000	

It will be noted from the above tables that the total for June and July, 1916, showed a marked decrease from those of previous months.

Investigations for the Government nitrate plant are being made by Colonel Newcomer and Major Kelly, Corps of Engineers, so far as all questions regarding the proposed site of the plant and its construction are concerned. A committee representing the Nashville Section of the Engineering Association of the South is to urge the selection of the Muscle Shoals site on the Tennessee River. Prof. W. G. Waldo, of Vanderbilt University, is the Secretary of the committee.

Chemical Engineer and Manufacturer

Vol. XXIV.

SEPTEMBER, 1916.

No. 3.

PUBLISHED MONTHLY by the MYRON C. CLARK
PUBLISHING CO.,

608 S. Dearborn Street, Chicago

*Entered as Second Class Matter, Aug. 19, 1907, at the Post Office
at Chicago, Illinois, under Act of March 3, 1879.*

Subscription—United States, Cuba and Mexico \$2.00
Extra postage to Canada 25c a year; to foreign countries 50c a year.
Remittances may be made by check, draft or money order in favor of
CHEMICAL ENGINEER AND MANUFACTURER

All communications should be sent to CHEMICAL ENGINEER AND
MANUFACTURER, 608 S. Dearborn Street, Chicago, Ill.

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FOREIGN DYE PRODUCTION.

European dye companies have recently taken steps of much interest to American manufacturers. The two main groups of producers of aniline dyes in Germany are stated to have been consolidated with a capital stock of \$100,000,000, the stock exchange value of which is said to be in excess of quarter of a billion dollars. Under the new combination, it is understood, the companies will exchange manufacturing processes and experiences, and each product will be manufactured by at least two works. In the past these firms have concealed from each other many of their processes. It is quite evident that this new combination will have great resources at its command.

Dye producers in Great Britain also have not been idle. The British Dyes Co.'s lately issued share and loan capital shows a total of \$9,643,000, an increase of more than \$2,000,000 over July, 1915. The supplies from other company's will be greatly increased, and a research department has been established in charge of Prof. W. H. Perkins. A provisional agreement has been entered into with the Syndicat National des Matiers Colorantes, a French company under support of the French Government, providing for a complete exchange of knowledge and processes and for the formation of an inter-allied company to establish co-operation.

THE CARGO OF THE DEUTSCHLAND.

The dye cargon of the Deutschland has been considerably reduced. First press reports set it at 1,000 tons, later it was 280 tons, and now according to the Oil, Paint & Drug Recorder the net contents of the 3,042 cases of aniline colors is about 125 tons. In a further discussion of the subject the Recorder states:

Included in the cargo are known to have been many colors not made in this country, specialties for use in both the cotton and the woolen industry, yet it is known that, despite persistent offerings, many of the manufacturers in these lines have refused even to consider a purchase. This is for two reasons. The first is that the asking price in many instances is from ten to twelve times the normal asking figure—dyes retailing before the war at from 35c to 45c being quoted at from \$4.00 to \$5.00, and even as high as \$9.00 and \$10.00 a pound. The second reason is that many American manufacturers—notably in the woolen and cotton print trades, and also in wall papers, etc.—formerly necessitating the use of anilines, have so adjusted their lines of goods that, with the aid of Amer-

ican dyestuff makers, they are getting along about as well as under normal conditions. It is generally held that were it not for the fear of German cut-throat competition after the war American dyestuffs manufacturers could so branch out and develop that in time all requirements would be met through domestic production.

There are two openly avowed reasons for the comparatively high price quotations made upon Deutschland anilines—the unusual degree of concentration of the dyes themselves and the remarkably high freight rate. It is claimed that many of these dyes are from $2\frac{1}{2}$ to 12 times as concentrated as any dyes heretofore sent to or produced in this country, a statement to which prominent American dye manufacturers take immediate exception as a commercial impossibility, on the ground that, while concentration of twice or twice and a half times the usual degree is possible, that of 10 or 12 times could not be brought about by any process within their knowledge.

As for the freight rates demanded and obtained—and it is openly asserted that the submersible's owners intended to get the cost of the vessel out of her first trip—it is said, on the authority of one of the consignees, that the rate charged was eight times the buying price of the dyes in Germany prior to loading. Even at the 35-cent to 50-cent a pound prices prevailing prior to the war, this would mean a direct freight charge of from \$2.80 to \$4 a pound, exclusive of insurance, warehouse charges, packing, carriage, truckage and all the other incidentals.

THE NEW U. S. PHARMACOPOEIA.

The new U. S. Pharmacopoeia, which will be issued this month, will contain a number of changes. In a recent paper Professor L. E. Sayre, Director of the Kansas State Drug Laboratory and a member of the Committee of Revision of the U. S. Pharmacopoeia, gives some details of the work of the committee. The new edition will make definite statements as to what will be considered as official and any potent drug or preparation on the market yielding more or less of said potency will not be recognized as official. This will result in great uniformity in the strength of our remedial agents.

Many new determinations have been made of a chemical character so that chemists will be able to detect adulterations with greater facility. For example, all of the crude drug products have been microscopically described and the elements in drug powders have been so completely identified and described that the laboratories, which have the responsibility of executing the law governing the sale of these agents, will have a satisfactory means of identifying the pure authentic material and will be able with greater facility to detect adulteration.

Among the important data which the revision com-

mittee has worked out is the yield of ash which individual drugs give. Each drug product has a definite amount of inorganic material, found in the ash. If this ash content is excessive the supposition may be entertained that adulteration or admixture has been practiced either unintentionally or otherwise. An undue amount of earthy material has been often shipped with crude material, thus increasing weight and diluting the article; this earthy material follows the drug to the mill and is unperceived in the powder—a standard for "ash content" is therefore a necessary determination for authentic material.

Every official drug has been carefully analyzed for ash content and the same recorded in the new revision as part of the standard for that particular drug. For example, belladonna leaf has an ash standard of 20 per cent, while the root is stated to have not more than 7 per cent of ash content.

One of the most pronounced improved features of the new pharmacopoeia is connected with the second part of the work, which deals with reagents and tests. Here is found the expert work of the committee.

FOREIGN ECONOMIC ALLIANCES.

The National Foreign Trade Council will issue shortly a report upon the European economic alliances and their effect upon the trade of the United States.

The study will deal with the purpose of the economic alliances projected by both groups of belligerents as outlined by European statesmen and the press. An analysis of the European treaty fabric partly disrupted by the war and the elements affecting its restoration and possible modifications of European tariff policy are to be features of the report, which is to be expository rather than argumentative. It is designed to make public facts as to prospective changes of policy in other parts of the world with which the United States has a large interchange of commodities. An elaborate analysis of the commercial interdependence of the countries of Europe and the United States is made to show the chief sources of supply and destination of exports from this country.

Among other features of the present situation which are studied to determine the probable effect on the United States are the economic alliances already existing, the degree to which "war after war" may be established, and the bearing of tariff navigation and financial changes upon our prosperity.

The pamphlet will give considerable attention to the evolution of European commercial policy, the European treaty situation before the war, the tariff system previously in force and an analysis of ante-bellum trade in Europe. In discussing the effect upon the United States a study is made of the trade interdependence of the British colonies, the chief European nations and the United States, and treaty guarantees as to shipping.

WATER SOFTENING CALCULATIONS.

By F. W. BRUCKMILLER.†

The calculation of chemicals for softening water from an analysis is often quite confusing to the beginner and concise statements regarding same are lacking, so it might not be out of place to take up in detail one or two methods that are useful.

We will first treat the case where a complete mineral analysis of water is made, i. e., SiO_2 , Fe, Al, Ca, Mg, SO_4 , Cl, NO_3 , HCO_3 and CO_2 are determined. Two things are necessary to keep in mind. First, the meaning of equivalent weight; and second, the fact that the sum of the equivalents of positive ions must equal the sum of the equivalents of negative ions.

An equivalent weight of a compound is its combining weight divided by the valence of the highest valent ion. Thus, equivalent weight of CaCO_3 is 100 divided by 2 or 50; for MgSO_4 , 120 divided by 2 or 60; for Na, 23; Cl, 35.45. In order, then, to convert a given weight of these substances into equivalent weights, we divide by their equivalent weights, or multiply by the reciprocal of them. The latter is a more convenient operation, so in all water softening calculations, we make use of the reciprocals of the equivalent weights instead of the equivalent weights themselves.

Table I contains the reciprocals of the equivalent weights of the most common elements found in water:

TABLE I.		
Positive radicals.	Reciprocal equiv. weights	Negative radicals.
Ferrous Iron (Fe)...	.0358	Carbonate (CO_3).....
Aluminum (Al).....	.1107	Bicarbonate (HCO_3)..
Calcium (Ca).....	.0499	Sulphate (SO_4).....
Magnesium (Mg).....	.0822	Chlorine (Cl).....
Sodium (Na).....	.0435	Nitrate (NO_3).....
Potassium (K).....	.0256	
Hydrogen (H).....	.992	Carbon Dioxide (CO_2)..

If we express the results of our analysis in parts per million, and then use the factors given in Table I, we will get so-called milligram equivalents. If the results are in grains per gallon, we will get grain equivalents. Since the Standard Methods of Water Analysis recommends the use of parts per million (p. p. m.) we will derive the formulae in those terms first.

The amount of chemicals necessary to soften a water, is reported as pounds per 1,000 gals., so to convert milligram equivalents of the substance to be removed to these terms, we use the following general formula:

$$\text{Lbs. of (A) per Mg} \\ 1,000 \text{ gallons} = \text{Equiv.} \times .05841 \times 1,000 \times \text{Equiv.}$$

7,000

weight (A) in which .05841 is factor to change p. p. m. to grains per gallons; 7,000 grains in a pound; 1,000 is number of gallons; and (A) the chemical to be used.

The substances used in water softening are lime and soda ash. In this process of softening, H^+ is changed to water, Ca^{++} , Mg^{++} , Fe^{+++} and Al^{+++} are removed as precipitates; the HCO_3^- and CO_3^{--} are changed to carbonates and H_2O and all CO_3^{--} removed as precipitate. The calcium added as CaO as well as that in the water is removed as CaCO_3 . The magnesium and iron are removed as hydroxides. The sodium added as Na_2CO_3 remains in solution as does the chlorine, sulphate and nitrate.

The reactions which occur are:

- (1) $\text{Fe}^{+++} + 2\text{OH}^- = \text{Fe}(\text{OH})_2$
- (2) $\text{Al}^{+++} + 3\text{OH}^- = \text{Al}(\text{OH})_3$
- (3) $\text{Mg}^{++} + 2\text{OH}^- = \text{Mg}(\text{OH})_2$
- (4) $\text{Ca}^{++} + \text{CO}_3^{--} = \text{CaCO}_3$
- (5) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
- (6) $\text{HCO}_3^- + \text{OH}^- = \text{CO}_3^{--} + \text{H}_2\text{O}$
- (7) $\text{CO}_2 + 2\text{OH}^- = \text{CO}_3^{--} + \text{H}_2\text{O}$

From this it is seen that one equivalent of OH^- or CaO or $\text{Ca}(\text{OH})_2$ is necessary to remove an equivalent of Fe, Al, H, Mg, HCO_3^- and CO_2 . Calculating the results of an analysis therefore, to milligram equivalents and using formula I, we get Formula II for pounds of lime CaO (90%) necessary to soften 1,000 gallons of H_2O .

$$\text{II. Lbs. CaO (90\%)} = .26 [(\text{Fe}^{+++}) + (\text{Al}^{+++}) \\ + \text{per 1,000 gallons } (\text{Mg}^{++}) + (\text{H}^+) + \\ (\text{HCO}_3^-) + (\text{CO}_2)]$$

Magnesium is removed as $\text{Mg}(\text{OH})_2$, as shown by (3) and is therefore taken care of by lime. The calcium is removed as CaCO_3 (equation 4), so that if not enough CO_3^{--} results from HCO_3^- or CO_2 by action of lime, more must be added as Na_2CO_3 , so all the calcium will be removed. In other words, this equation must be true, expressed in equivalents:

$$(8) (\text{CO}_2) + (\text{CO}_3^{--}) + (\text{HCO}_3^-) = \\ (\text{Ca}^{--}) + (\text{CaO added for other cations}) \\ = (\text{Ca}) + (\text{Fe} + \text{Al} + \text{Mg} + \text{H})$$

The lime reacting with CO_2 and HCO_3^- gives CO_3 to react with any Ca, Fe, Al, Mg or H, so does not occur in equation 8.

Expressing these facts in an equation, we get:

$$\text{III. Pounds Soda Ash (95\%)} = .465 [(\text{Fe}^{+++}) \\ + (\text{Al}^{+++}) + (\text{Ca}^{++}) + (\text{Mg}^{++}) + \\ \text{per 1,000 gallons } (\text{H}^+) - (\text{CO}_3^{--}) - \\ (\text{HCO}_3^-)]$$

If the sodium content of a water has been accurately determined the quantity of soda ash can be obtained by this reasoning. Since the sum of the equivalent of cations must equal the anions, and since all the calcium and magnesium is to be removed, enough Na must be added to unite with all the chlorides, sulphates and nitrates in the water. From this we get equation

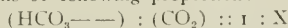
$$\text{IV. Lbs. Na}_2\text{CO}_3 (95\%) = +.465 (1\text{SO}_4 + \text{Cl} + \\ 1,000 \text{ gallons} \\ \text{NO}_3) - \text{Na})$$

†Chemist Water and Sewage Laboratory, University of Kansas, Lawrence, Kan.

This equation can be used also if Na is reetermined by difference but the results are not so accurate.

Complete analyses are not always made. Rapid methods are used for determining the temporary or carbonate hardness and magnesium and the non-carbonate hardness. Under the former are included alkalinity and carbon dioxide determination, while under the latter is contained the determination of calcium and magnesium compounds other than bicarbonates by means of "soda reagent." If these are the only results obtained, the calculation for lime and soda ash is as follows:

The total Mg is determined by a short, rapid method (Standard Method H₂O analysis (1912) p. 35). All the bicarbonates are calculated to CO₂ by means of following proportion:



and this added to the free CO₂ present. According to equation 7, it requires one equivalent lime or OH for each CO₂ and according to 3, one equivalent for each Mg, therefore equation (II) simplifies to

$$V. \text{ Lbs. Ca(OH)} (80\%) = .260 [(\text{CO}_2) + (\text{Mg})]$$

per 1,000 gallons

From the "soda reagent" determination, we get incrustants in terms of CaCO₃, which is converted into equivalents by multiplying by .02 (1/50). This value takes place of the values in brackets in equation III. VI. Lbs. 1,000 Na₂CO₃ (95%) = .465 × (CaCO₃) gal.

Studying Industrial Conditions in France.

An American commission is now in France making a scientific study of industrial conditions in that country to determine the most advantageous method whereby resources in the United States may be made to cooperate in the reconstruction that will follow the war.

Following is a partial list of the personnel of the commission: William Wallace Nichols, chairman, assistant chairman Allis-Chalmers Mfg. Co., Inc.; E. V. Douglass, general secretary, Secretary American Mfrs. Export Assn.; A. B. Farquhar, president, A. B. Farquhar Co., Ltd., York, Pa.; J. E. Sague, former vice president, American Locomotive Co.; F. J. LeMaistre, (B. S., M. E.), Consultant, E. I. du Pont de Nemours & Co., Wilmington, Del.; Curt G. Pfeiffer, vice president, Geo. Borgfeldt & Co.; John R. MacArthur, MacArthur Bros., 120 Broadway; Dr. C. O. Mailloux, consulting engineer, 20 Nassau street; E. A. Warren, vice president, Universal Winding Co., Boston; Samuel W. Fairchild, vice president, Fairchild Bros. & Foster, 76 Leight street; Noble Foster Hoggson, president, Hoggson Bros., Inc., contractors, 485 Fifth avenue; J. G. Butler, Jr., director, Commercial National Bank, Youngstown, Ohio, vice president, Brier Hill Steel Co.; E. E. Russell, J. I. Case Threshing Machine Co., Racine, Wis.; A. Swasey, president, Warner & Swasey, Cleveland, Ohio; George Burdett Ford, member of George B. Post & Sons, 101 Park Avenue,

FRENCH SPECIFICATIONS FOR SHELL STEEL.*

The specifications covering purchases recently made, and yet to be closed, of round shell steel and round-cornered billets for the shells of the largest diameters for the French Government, are substantially in full as follows:

The bars are to be of rolled or forged steel of the best quality and manufactured by the "acid, basic open-hearth process or electric furnace process," homogeneous throughout, and free from seams, flaws, piping and porosity.

PHYSICAL TESTS FOR EACH HEAT.

Four test bars shall be taken from a portion of the head end of the first bar of one ingot close to the discarded portion, or from a small ingot poured in the middle of the pouring, having such a section as to have the same reduction of area between ingot and test bars, as between the regular ingot and the bars contracted for. The test bars after forging, machining and heat treating are to be finished to the following measures: diameter, 13.8 mm. (0.543 in.); length between marks, 100 mm.

Said test bars are to be annealed, say heated to a temperature between 875 and 950 deg. C. for 20 min. and slowly cooled off in ashes or lime. Out of these four annealed bars, two are to be heated 20 min. at 825 to 875 deg. C., then quenched in water at 15 to 24 deg. C. (60 to 75 deg. Fahr.), and heated again 20 min. at 500 to 536 deg. C. in a bath of molten metal.

Such treatment will give two bars, *b*, annealed and two bars, *c*, temper-drawn after quenching. The bars *b* and the bars *c* to be treated for tensile results, as follows:

	Bars <i>b</i>	Bars <i>c</i>
Breaking load per sq. mm.	55 to 65 kg.	85 to 105 kg.
(Breaking load per sq. in., lb.)	78,000 to 92,500	120,000 to 150,000
Elongation, minimum on		
100 mm.	18 per cent	9 per cent

Occasionally the inspector will take out of the finished material two test bars, which will be treated as above and tested either in the plant, or in another place for verification, at the convenience of the inspector, it being understood that the ordinary variation between head and foot of ingot is to be allowed for.

CHEMICAL COMPOSITION.

Chemical specifications are to be subordinated to physical tests, which are to govern. Inspectors are instructed to accept slight alterations to the subjoined requirements when physical tests and soundness of steel prove to be satisfactory. Composition of each heat is to be determined by analysis of a sample cast at about mid run. Apart from the iron, the following chemical elements may occur on the percentage shown:

	Min.	Max.
Carbon, per cent.....	0.30	
Silicon, per cent.....	0.15	0.25
Manganese, per cent.....	0.50	0.80
Phosphorus, per cent.....	0.03	0.08
Sulphur, per cent.....		0.05

*From the Iron Age.

DISCARD.

The ingots must preferably be top-poured and a discard of 28 per cent off the top end and a discard of 4 per cent off the foot end of each ingot must be rejected. Such discards must be made after the ingots have been rolled into blooms or bars. Said minimum proportion of ingots, blooms or bars to be discarded is not allowed to be reduced without a written authorization from the head of the French Commission, and no reduction will be considered by him until the maker has given satisfactory proofs, through special inspection of the discards for at least fifty consecutive heats, made upon maker's application, that a new figure can be proposed. The new per cent of head discard which may be agreed upon by the head of the French Commission upon due reports of the inspection, will be thereafter a compulsory minimum for all the following heats of the same fabrication. The new per cent will not be in any case under 20 per cent, except when a special process of casting with sinkhead on inverted molds or similar is used.

In case the current fabrication should show that the adopted per cent of discard is not sufficient to remove practically all piping and porosity from the mill products, a new higher constant proportion of discard shall be adopted in order to obtain the result.

In order to ascertain whether the steel is free from piping, there will be left in the center of the section, between the discard and the utilizable part of the ingot, a core, which shall be broken cold in the presence of the inspectors. If the first discard is not sufficient, there will be made one or several others, under the same conditions, and until complete disappearance of the defects. This operation may be made at the choice of the contractor, either on the ingot, or on the bars rolled completely, or not, up to their final size.

For the large section bars (diameter of 200 mm. and upward) it may furthermore be exacted that the hot or cold sawing of each bar shall leave in the center of the section, a core to be fractured cold, in order to examine the grain of the metal and to make sure of the absence of any piping. This cold fracture is to be made in the presence of the inspectors. The inspectors shall also have at any time the right to have cold broken, for examination of each ingot, one bloom or one bar to be selected in any part of the ingot, and particularly when the ingots are bottom poured and likely to be spoiled by secondary piping. The inspector shall in addition have the right to have, for each heat, a maximum number of eight parts of the bar acid pickled or etched to verify at sight the condition as to porosity and piping and as to surface defects.

CONDITION OF BARS.

The bars are not to be submitted to any heat treatment; only the ordinary good straightening of bars on the cooling bed is called for. But they must be clean enough from scale after rolling so that the surface of the bars may be thoroughly inspected.

SELF-LUMINOUS PAINT.*

By W. S. ANDREWS.†

Soon after the discovery of radium by the Curies in 1898 certain fluorescent and phosphorescent mineral compounds were found to be so sensitive to the radioactivity of this element that they show luminescence when only brought near it, actual contact being unnecessary. A fine quality of zinc sulphide known as Sidot's blende proved to be the most responsive.

Sir William Crookes by the invention of his ingenious spinthariscopes brought this phenomenon of radioactive luminescence prominently before the public eye. This device consists of a little dark chamber enclosing a disk of cardboard that is coated with zinc sulphide. A small wire is fixed above the disk so that one end of

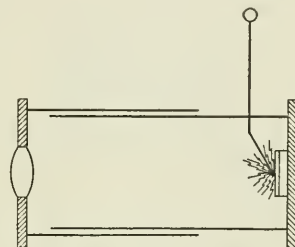


Fig. 1—Diagram of Spinthariscopes.

it is very close to the sulphide but not touching it and a microscopic speck of a salt of radium is attached to this end of the wire. When this combination is observed through a magnifying lens of proper power, the zinc sulphide is seen to be perpetually scintillating with innumerable little stars in the vicinity of the radium. This remarkable appearance is caused by the alpha rays that are discharged from the radium with tremendous velocity, some of which bombard the sulphide like atomic cannon balls, every hit producing a flash of light on the target. The accompanying diagram, Fig. 1, shows the construction of this wonderful device in its simplest form.

A next obvious step was to mix a very minute amount of radium salt with finely powdered zinc sulphide so that it might be combined with a suitable adhesive and used as a *self-luminous paint*. For a long time this paint was looked upon only as an interesting scientific curiosity but during recent years it has been applied in various useful ways to make small objects constantly visible in the dark. For example, it is now used extensively on the hands and dials of watches and clocks, making it easy to tell the time in total darkness; also on the pointers of aeroplane and prismatic compasses and other instruments. One of its most recent and convenient applications is on electric switch buttons, drop chain sockets, etc., thereby guiding a person directly to the switch in a dark room.

*From the General Electric Review.

†Consulting Engineering Department, General Electric Co.

This radio-active self-luminous paint must not be confounded with an article that has been on the market for many years under the name of "Balmain's luminous paint," which was invented by Prof. Balmain of the London University about the year 1875. The base of the Balmain paint is a special preparation of phosphorescent calcium sulphide, and it requires the excitation of a strong light to make it shine. It absorbs the luminous radiation and then emits it again as a soft phosphorescent glow which gradually fades away so that in the course of a few hours it ceases to be visible until again excited to phosphorescence. The *self-luminous* radio-active paint differs entirely from the above in containing within itself its own exciting power, so that it continues to shine indefinitely even when kept in perpetual darkness.

The question is sometimes asked, "How long will the self-luminous compound maintain its brightness?" According to recent research, the "half-period" decay of radium is 1,750 years. Based on this assumption, and taking for example one gram of radium to start with, one half of this will disappear by spontaneous decomposition in 1,750 years, leaving half a gram. During the next period of 1,750 years one half of this remainder will disappear, leaving one quarter gram and so on. It is thus evident that, for all practical purposes, the life of the radium content may be considered unlimited. *Not so, however, with the zinc sulphide*, the quality of which in itself is subject to considerable variation according to its purity and the method of its preparation. There appears to be a *certain amount of luminous quality* locked up, so to speak, in the zinc sulphide. This quantum of light-producing ability may be liberated and used up quickly and with high intensity by strong excitation, or slowly and with a lower intensity by a weaker excitation. Therefore, assuming the use of a uniform quality of zinc sulphide, the useful life of a very bright self-luminous compound will naturally be shorter than that of a compound showing a weaker luminescence, and the intensity of luminescence will depend on the percentage of radium element mixed with the zinc sulphide.

An incandescent lamp may be taken as a familiar illustration of this argument. We may compare the voltage used on the lamp to the radium, and the filament to the zinc sulphide. We all know that an incandescent lamp operated at a voltage well below normal has a very long life and, vice versa, when it is operated at a voltage much higher than normal its life is short. These results are practically parallel with the results which obtain in connection with a self-luminous paint. The *normal* voltage for an incandescent lamp is arbitrarily decided by conditions under which it will produce a satisfactory light for a reasonable number of hours, and these same conditions may be applied to the consideration of a proper degree of brightness for self-luminous radium-zinc compounds. If a compound containing, say, 100 micrograms of radium element per gram of zinc sulphide has a useful life of twenty years, it is reasonable to

infer that by doubling the radium content the luminescence will be increased about two-fold; but the useful life will be halved, or reduced to ten years.

The satisfactory luminescent intensity of a radio-compound will depend largely on the purpose for which it is used, this also involving the area of the luminous surface employed, so that no fixed standard of light per unit of surface can be adopted. For Army and Navy purposes the United States Government calls for a guarantee on self-luminous paint that it shall maintain an undiminished luminosity for two years. In view of this very moderate demand a high grade quality may be safely used.

It is well known that the phenomenon of radio-activity is not confined to radium. A product of thorium, known as radio-thorium, is intensely radio-active, but it has a much shorter life than radium, its half-period of existence being estimated at only three or four years. Meso-thorium, from which radio-thorium is evolved, is a by-product of the incandescent gas mantle industry and on account of its relative cheapness as compared with radium it is now being used extensively either by itself or combined with radium in the production of self-luminous paints.

There is a difference of opinion in regard to the merits of the radio-thorium paint and paint that is energized entirely by radium, but both compounds will probably find their appropriate applications in the future.

Sugar in Cuba and Java.

According to a statement issued the latter part of August by the Federal Sugar Refining Co., unprecedented prosperity in the sugar industry because of the record high prices is causing extraordinary preparations in the cane growing countries for next year's crop of sugar. Java, according to cable advices, plans to increase its crop 250,000 tons, or 20 per cent, and in all sugar producing sections not at war there is the greatest activity. It is stated that twelve new mills are planning to operate next season grinding Cuba's 1917 crop, which will begin to come in about the middle of January.

The new centrals include that of the Punta Alegre Sugar Company with 300,000 bags capacity. E. F. Atkins, of Boston, a former vice-president and director of the American Sugar Refining Company, is president of this concern. Other large enterprises are the Adelaida, with a possible outturn of 200,000 bags; Alto Cedro with 180,000; Tacajo with 170,000; Central Oriente with 100,000; Algodones with 100,000, and the Miranda with 150,000 bags capacity. The last named has just been organized by the Warner Company of New York.

It is not expected that any of these plants will grind more than a third to a half of their capacity next season, but they may have an important effect in augmenting the available supply of Cuban sugar in 1917.

A NEW FORM OF VISCOSIMETER.

A new form of viscosimeter has been devised by H. C. Hayes, Professor of Physics, and G. W. Lewis, Assistant Professor of Engineering, at Swarthmore College. The following description of the apparatus is taken from a paper presented at the spring meeting of the American Society of Mechanical Engineers by Messrs. Hayes & Lewis and printed in the Journal of the Society.

The viscosimeter operates in accordance with the principle that a solid body having a surface of revolution experiences, when suspended in a rotating liquid, a torque which is proportional to the viscosity of the liquid. The instrument is shown diagrammatically in Fig. 1. The specimen, *S*, is contained within a cylindrical chamber which is caused to rotate uniformly by a motor, *M*, through a worm drive, *R*. A cylinder, *C*, is suspended within the specimen by a thin steel wire, *H*, so that the axis of the rotating liquid coincides with the axis of the cylinder. The specimen chamber is provided with a cap, *I*, so shaped that the

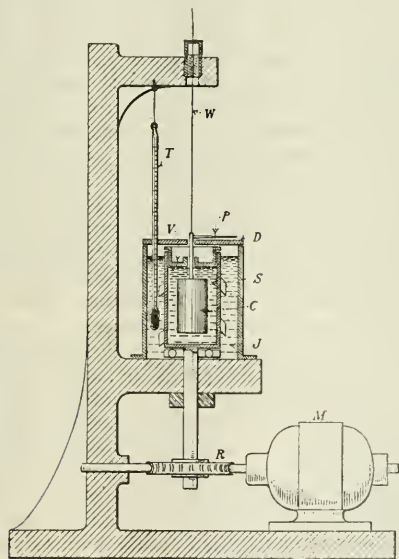


Fig. 1—The New Viscosimeter.

excess liquid can overflow when the cap is seated and thus give constant conditions within the chamber. The specimen chamber is surrounded by an oil jacket, *J*, in which a thermometer, *T*, is suspended. The jacket oil may be brought to any desired temperature by means of a heating coil, or a side coil not shown in the diagram. The cover, *D*, of the jacket chamber is provided with a scale which is marked in degrees or may be calibrated to read off directly, through the deflection of the pointer, *P*, the viscosity in terms of a standard liquid. The specimen chamber and the suspended cylinder are both made of copper to insure

constant temperature throughout the specimen and the outside of the specimen chamber is provided with blades which keep the jacket oil thoroughly mixed as the chamber revolves and thereby exposes the latter to a uniform temperature. This is an important factor toward insuring constant temperature throughout the specimen.

The experimental work has shown that the temperature of the specimen is uniform to within a small fraction of a degree. Moreover, the temperature of the specimen follows the temperature of the jacket oil so closely that the temperature-viscosity curve can be taken while the temperature is slowly raised or lowered. This proves to be a great saving of time.

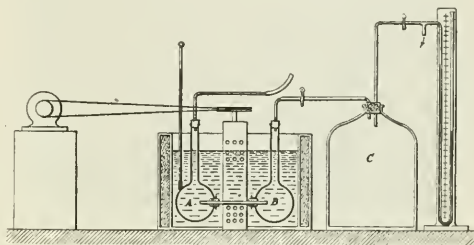


Fig. 2—Capillary Tube Method.

It also saves labor, for one does not need to stand by the instrument continually. The deflection of the pointer is at any instant a measure of the viscosity, so all that is required is to take simultaneous readings of temperature and deflection at intervals during the heating or cooling process.

EXPERIMENTAL RESULTS.

To test the accuracy of this viscosimeter, the temperature-viscosity curve was found for a light and a medium gas engine oil by the capillary tube method, the apparatus for which is shown in Fig. 2. The oil was drawn from vessel *A* to vessel *B*, and vice versa, by connecting each in turn with the partial vacuum chamber, *C*. These vessels were submerged in a thermostat which could be maintained at any desired temperature. The results, in terms of the viscosity of water at 20° C., are given by the points enclosed in circles for curves 1 and 1a, Figs. 3 and 4, the latter referring to the lighter oil. The viscosity of these same oils as given by the new meter is represented on curves 1 and 1a by the points enclosed, in squares. The agreement between the two methods is almost perfect.

The viscosity of these oils as given by a meter of the short capillary type, is given in curves 2 and 2a. Curves 3 and 3a give the viscosity of these oils as obtained with a meter of the orifice form. As predicted, the results given by the short capillary type are much too low (on the oils tested about 100 per cent too low), and the results given by the orifice type are still lower.

It is claimed that the new viscosimeter of the non-flow type described has the following advantages:

1. It gives values for the viscosity which are in

agreement with those given by the standard capillary tube method.

2. During a series of tests at various temperatures, the oil is not handled.

3. The sensitiveness of the instrument can be made anything desired by changing the speed of rotation of the specimen or by using suspension wires of various diameters.

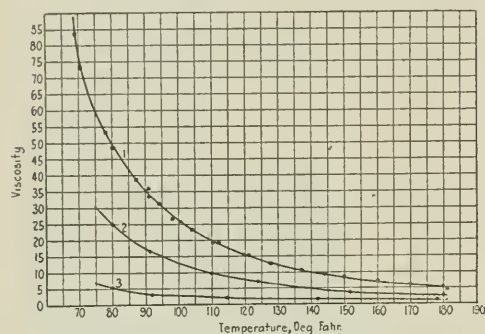


Fig. 3—Viscosity Curves for Medium Gas Engine Oil.

4. The density or change in density is not a factor in computing the results, in fact the instrument may be graduated to read off the viscosity directly.

5. The viscosity of liquids which contain particles in suspension can be measured, and the operation of the meter is independent of the color of the specimen.

6. The temperature-viscosity curve can be taken

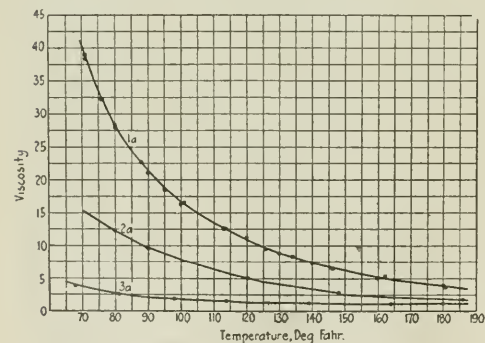


Fig. 4—Viscosity Curves for Light Gas Engine Oil.

with a fair degree of accuracy while the temperature is rising or falling, as the temperature of the specimen follows the temperature of the jacket so closely.

7. The personal error which arises in determining time intervals with a stop watch is removed.

8. The instrument is simple, rigid and self-contained. It has no separate parts to get lost or glass parts to get broken.

POTASH AS A BY-PRODUCT IN THE CEMENT AND IRON INDUSTRIES.*

By ERNEST F. BURCHARD, United States Geological Survey.

The Manufacturers Record has already, by means of a number of timely articles, attracted wide attention to the possibilities of profitable potash recovery in two of the nation's greatest manufacturing industries. Four Federal bureaus have begun inquiries or studies bearing on the subject, and it is evident that its importance to the nation will insure its being thoroughly investigated by public and private agencies.

POTASH FROM CEMENT MANUFACTURE.

The collection or elimination of dust in the cement plant is one of the most important problems in cement manufacture at present, and incidental to the study of this problem the year 1915 witnessed an awakening of interest on the part of several cement companies to the possibility of recovering potash as a by-product in cement manufacture. The pioneer in this field was the Riverside Portland Cement Co., the plant of which is at Riverside, Cal. The early efforts of the Riverside Company, which employs the Cottrell electrical precipitation process,† were directed rather toward precipitating waste dust than toward recovering potash, but the company soon discovered that, although the raw mix contained only about 0.2 per cent of potash, the dust contained potash in considerable quantities, and a large portion of it is now being recovered. Since the supply of potash from Germany has been cut off, the Riverside Company has contracted for the sale of its potash at prices that yield large returns on the investment for the dust-collecting equipment.

The Western Precipitation Company of Los Angeles, Cal., controls the license for all applications of the Cottrell precipitation process to cement manufacture. This company reports that it has made analyses of a large number of samples of raw mix used by cement mills in the United States, and finds that the potash content of the raw mix used at Riverside is much lower than the average. This affords encouragement for the hope that the problem of potash recovery may be more generally undertaken by cement manufacture in the near future.

The high prices for potash that have prevailed since the shortage began to be felt have, of course, stimulated many and diverse efforts to discover or devise a domestic source of potash, and the first plant in the South to follow the lead of the Riverside plant is that of the Security Cement & Lime Co., at Security, near Hagerstown, Md. The limestone used by the Security Company in making Portland cement contains more than the average percentage of potash (K_2O), a fact which lends encouragement to the effort to recover it

*From the Manufacturers Record, in which it is published by permission of the Director of the United States Geological Survey.

†Schmidt, W. A., Cottrell processes of electrical precipitation; Canadian Min. Inst. Trans., Vol. 18, pp. 110-133, 1915.

at this plant. A commercial output of potash is now being obtained here.

A description of the plant at Security, Md., has been published in the Manufacturers Record.[‡]

A process in which it is proposed to reverse the order of products and make cement as a by-product from potash has been outlined in recent publications.[§]

After several years of investigation and experimentation a commercial plant designed to produce 20 tons per day of potash salts from feldspar and limestone, with hydraulic cement as a by-product, is being constructed at Buffalo, N. Y. A yield of 1,000 barrels per day of cement is expected. Crushed limestone and feldspar or other potassium silicate rock are thoroughly fused in a furnace and maintained at a temperature of 1300° C. until the potassium salts are volatilized. The volatilized salts pass into the furnace gases which are utilized for producing steam in the waste heat boilers. When these gases have cooled to about 400° C. they are passed through Cottrell collectors, which separate out most of the potash salts, and the remainder are saved by a washing process. The molten mass from which the potash salts have been volatilized flows from the furnace, is granulated, and treated with solutions of certain salts. This granulated clinker is then ground and mixed with a small percentage of gypsum or other material for regulating the set, and is then ready for use as a cement. This is known as the Brown process, the patents having been issued to H. E. Brown.

The Portland cement industry in the United States showed a phenomenal growth from 1895 to 1913, but

in 1914 it experienced a slight check, and made only a slight recovery in 1915, so it seems very fortunate that just at this time the possibility of recovering potash as a by-product in cement manufacture should be realized. It means a new stimulus to a giant industry that otherwise seemed to have about reached its maturity. It has been suggested that in the future new Portland cement plants may be located at places where the limestone carries the highest percentages of potash. It is probable that location with respect to supplies of the basal raw materials, limestone and clay, shale, or blast-furnace slag, fuel, good shipping facilities and proximity to markets will continue to be the most important features, but between two localities where the conditions are about on a par the presence of potash in greatest quantity in the raw materials would undoubtedly prove the controlling factor, and it may develop into still greater importance. There is, however, the possibility that processes will be perfected whereby materials high in potash, such as feldspar, sericite and greensand, may yet be made to yield their potash in the portland cement kilns, and that it will prove more advantageous to bring them to the plant than to ship the more bulky cement a greater distance.

CEMENT MANUFACTURE IN THE SOUTH.

In order to show the especial bearing of this discussion on the cement industry in the Southern States, it is essential to introduce some statistics concerning the output and consumption of cement in the South, compared with those of the United States, to indicate the obvious commercial advantages possessed by many cement-producing localities in the South, and to outline some geological facts concerning the distribution of raw cement materials and fuels in the South.

[‡]Recovery of potash at Security cement plant: Manufacturers Record, May 11, 1916, pp. 44-45.
[§]Hydraulic cement is a by-product of potash plant: Cement and Eng. News, May, 1916, p. 114; also Concrete Age, May, 1916, p. 21.

PORTLAND CEMENT SHIPPED FROM MILLS IN THE SOUTHERN STATES, 1914 AND 1915.

	Active plants.		1914		1915	
	1914.	1915.	Barrels	Value.	Barrels.	Value.
Maryland, Virginia and West Virginia.....	4	4	2,793,036	\$2,449,493	3,166,721	\$2,584,044
Tennessee, Alabama and Georgia.....	5	5	2,577,099	2,409,588	3,099,770	2,343,426
Kentucky, Missouri, Oklahoma and Texas.....	12	12	8,339,372	8,541,481	8,089,860	7,832,135
Total.....	21	21	13,709,507	\$13,400,562	14,350,351	\$12,759,605
Total of United States.....	111	109	86,437,956	80,118,475	86,891,681	74,756,674
Southern States' percentage.....	19.	19.	16.	17.	17.	17.

ESTIMATED PER CAPITA CONSUMPTION OF PORTLAND CEMENT IN THE SOUTHERN STATES AND IN THE UNITED STATES AND OUTLYING POSSESSIONS IN 1914 AND 1915.

State.	Population (estimated).	1914		1915	
		Consumption (shipments to States), Barrels.	Estimated consumption per capita, Barrels.	Consumption (shipments to States), Barrels.	Estimated consumption per capita, Barrels.
Alabama.....	2,269,945	517,405	.23	2,301,277	.17
Arkansas.....	1,686,480	400,607	.24	1,713,102	.16
District of Columbia.....	353,378	341,227	.97	358,679	1.23
Florida.....	848,111	460,974	.54	870,802	.55
Georgia.....	2,776,513	511,385	.18	2,816,589	.17
Kentucky.....	2,350,731	874,538	.37	2,365,185	.35
Louisiana.....	1,773,482	583,159	.33	1,801,306	.43
Maryland.....	1,341,075	1,624,180	1.21	1,351,941	1.01
Mississippi.....	1,901,882	206,782	.11	1,926,778	.11
Missouri.....	3,372,886	2,940,638	.87	3,391,789	.85
North Carolina.....	2,339,452	529,643	.23	2,371,095	.24
Oklahoma.....	2,026,534	508,233	.25	2,114,307	.32
South Carolina.....	1,590,015	176,693	.11	1,607,715	.17
Tennessee.....	2,254,754	802,711	.36	2,271,379	.32
Texas.....	4,257,854	1,821,628	.43	4,343,710	.40
Virginia.....	2,150,000	1,008,492	.47	2,171,014	.54
West Virginia.....	1,332,910	1,250,557	.94	1,359,474	.79
Total.....	34,626,011	14,558,852	.42	35,135,872	.41
Total for the United States.....	108,889,493.	84,298,151	.77	110,755,853	.76

Production.—Portland cement is manufactured by 21 plants, situated in 10 of the 16 Southern States. The output of these plants represents about 17 per cent of that of the United States as a whole. In the majority of the Southern States there was an increase in shipments of Portland cement in 1915 compared with 1914, and the net change for all the 10 producing States was an increase. This is encouraging as indicating a rapid recovery from a year of depression, and also because the percentage of increase was nearly 10 times greater than that of the whole United States. These data are shown in one of the accompanying tables.

Consumption.—The next thing to consider is what the relationship is between production and consumption of cement in the South. Statistics of shipments to Southern States show that in 1914 the South consumed about 850,000 barrels more cement than it manufactured, and in 1915 it took only 150,000 barrels more. Not a wide margin—not enough to warrant the building of a new cement mill without cutting into the trade of other established plants. But this is not all the table shows. It shows that the per capita cement-consuming power of the Southern States is as yet only about 54 per cent of that of the United States as a whole, or, where .76 barrel of cement is consumed per capita in the United States in 1915, the average per capita consumption of the Southern States is .41 barrel. This should afford encouragement to the cement manufacturer and the cement salesman as showing that there is room in this field for more educational work to show the advantages of using cement and concrete.

EXPORTS.

In 1915 the hydraulic cement exported from the United States to foreign countries, including the Philippines and the Panama Canal Zone, was 2,565,031 barrels, most of it Portland cement, valued at \$3,361,451 at the United States ports of shipment, an average of approximately \$1.31 a barrel. The quantity exported in 1915 was not quite 3 per cent of the total production of hydraulic cements. The exports have never been great, the largest quantity, that in 1912, having been only 4,215,532 barrels. The exports for 1915, however, showed an increase of nearly 20 per cent over those of 1914, and as this increase was due largely to greater exports to South American countries and the West Indies, it appears that the cement trade is expanding in the direction of the greatest promise, especially to mills in the Southern States that are convenient to tidewater. There were relatively large increases in exports to Brazil, British Guiana, Barbados, Jamaica, Trinidad and Tobago Islands, Chile, the Dutch West Indies, Ecuador, Mexico, Peru, Salvador and Uruguay. The building up of an export trade in Portland cement offers great possibilities to southern mills. That this has been recognized is shown by the fact that the Texas Portland Cement Co. early in 1916 completed a new mill on tidewater at Houston, Texas.

PORTLAND CEMENT MATERIALS IN THE SOUTH.

The distribution of cement-making limestone, clays and suitable kiln fuels in the Southern States has been discussed and illustrated by a map in an earlier issue of the *Manufacturers Record*,* so only a brief mention of these resources need be made here. The limestones suitable for making petroleum and natural gas occur in abundance in Oklahoma, Texas, Arkansas (early geologic) age, the softer chalks of Mesozoic (middle geologic) age and the little consolidated shell marls of Cenozoic, or comparatively late geologic age. The Paleozoic limestones are widely distributed through the Appalachian valleys of Maryland, the Virginias, East Tennessee, Georgia and Alabama, in the central portions of Kentucky, Tennessee and Texas, and the Ozark region of Missouri, Arkansas and Oklahoma. The chalky limestones are found in eastern Texas, northern Louisiana, southern Arkansas and in belts crossing the States of Mississippi, Alabama, Florida and extending into Tennessee on the northwest and Georgia on the southeast. The shell beds are found in the coastal plain region of Virginia, the Carolinas, Georgia and Florida. Beds of shale or clay are found in all the areas, some of them interbedded with limestones and other rocks, and some residual from the disintegration of limestone.

Bituminous coal areas border the limestone belts in the Appalachian States and in Missouri, Oklahoma and Arkansas. Lignite, possibly of use for steam fuel, is available in Texas, Arkansas, Louisiana, Mississippi and Alabama. Petroleum and natural gas occur in abundance in Oklahoma, Texas, Arkansas, Louisiana and West Virginia, and may be found in other states as a result of explorations in progress.

So, without going further, it is very apparent that the South possesses the potential resources for a greatly enlarged cement manufacturing industry, and if the chemists will study carefully these limestones, shales and clays, there is little doubt that many deposits will be found equally rich in potash as the beds at Security, Md.

As to the distribution of feldspar in the South, Katz reports that a belt extending southwest through Harford, Baltimore, Howard and Montgomery counties, Maryland, contains a great number of large, high-grade pegmatite dikes, which are quarried in many places, and which supply a large proportion of the feldspar consumed in the United States. The Piedmont province in Virginia, North Carolina, South Carolina, Georgia and Alabama and much of the Appalachian Mountain province are occupied by rocks in which pegmatite dikes are widely distributed. Some of these have been worked for feldspar, and many more have been developed for their content of kaolin,

*Burchard, Ernest F., *Portland cement resources and industry in the Southern States: Manufacturers' Record*, Mar. 27, 1913, Pt. 2, pp. 69-71.

†Katz, F. J., *Feldspar in 1915: Min. Res. U. S., 1915, U. S. Geol. Survey, 1916, pp. 48-49.*

mica and gem minerals; these latter give promise of supplying feldspar also. In Virginia an area in Bedford and Henry counties, and another in Amelia and Prince Edward counties, have been commercial producers of feldspar. In North Carolina the spruce pine district in Avery, Mitchell and Yancey counties annually produces a large quantity of feldspar. The regions of Iredell, Lincoln and Cleveland, and of Jackson, Macon and Swain counties are particularly promising for feldspar production. In South Carolina some feldspar has been produced in the neighborhood of Pacolet, in Spartanburg county. There has been no production of feldspar in Georgia or Alabama. In St. Genevieve county, in the Ozark regions of Missouri, there are pegmatite dikes containing feldspar of good grade, but there has been no commercial development in this region. In Llano and Burnet counties, Texas, there are pegmatite dikes which may become a source of feldspar. Not all these feldspars contain potash, but most of those that are mined are of the potash variety, and may contain up to 13 per cent K_2O .

ADVANTAGES POSSESSED BY THE SOUTH.

To summarize, the supplies of raw material are inexhaustible and most advantageously located; abundant supplies of high-grade fuel are closely associated with them; excellent quarrying and manufacturing sites are to be found along the railways and rivers; water supplies and water-power are abundant, and economical electric power is being developed. Transportation facilities, including river navigation and Atlantic and Gulf harbors, are being improved. Export trade has been facilitated by the opening of the Panama Canal, and now that to the by-products of cement manufacture, such as crushed rock and chemical limestone, may possibly be added the very valuable potash, there is, indeed, a bright future for cement manufacture in the South.

POTASH FROM IRON MANUFACTURE.

In the field of iron manufacture there is as yet no actual experience in the recovery of potash upon which to draw, as in the cement industry. The recent article by Charles Catlett† is, however, so replete with suggestions of great interest and promise to the chemist and metallurgist that the writer, who has been making studies of the iron-ore resources of the South for several years, feels that perhaps the way has at last been pointed out by which vast reserves of ore, whose grade is at present a little below par in a commercial sense, may be made of value. In pointing out the variability in iron-ore composition, Mr. Catlett makes the reassuring statement that the leaner, more siliceous ores are apt to be higher in potash. In support of this generalization Mr. Catlett cites certain analyses of gray iron ores near Talladega, Ala. The gray ores may well be suspected of carrying relatively high percentages of potash, because the gangue comprises certain metamorphic minerals which carry potash, such as feldspars and mica.

Unfortunately, there are few analyses sufficiently complete as to show the potash content in iron ore. Mr. Catlett mentions published analyses (source not given) which show between 1.50 and 2 per cent, and showing over 2 per cent [potash?]. The writer finds published† analyses of three samples of these gray ores which show the combined potash and soda to range from 1.57 to 2.11. Inasmuch as the feldspar present is largely a soda-lime feldspar, it is possible that there may not be as large a percentage of potash present as at first glance seems evident. However that may be, there is probably enough potash present to render the ore of great promise in this connection, particularly since there are large reserves of these gray ores still undeveloped.

The Clinton iron ore, a red hematite, is found in many parts of the United States. It occurs near Clinton, N. Y., whence its name; in Wisconsin, Missouri, in eastern Canada, and attains its greatest development in the Southern Appalachian region. This ore, of Silurian age, occurs in beds varying in thickness from an inch to 30 feet, interstratified with shale, sandstone and thin limestone.

Important deposits are found in southwest Virginia, east Tennessee, northwest Georgia and northeast Alabama. Among the localities where mining is active today are the Boones Path mines, in Lee county, Virginia; the LaFayette mines, in Campbell county; the Rockwood-Cardiff mines and the Chamberlain mines, in Roane county, Tenn.; the Estelle mines, in Walker county, Georgia; the mines at Attalla and Gadsden, Etowah county, and the many large mines of the Birmingham district, Jefferson county, Alabama.

Nearly all these are underground mines. In former years open-cut mining was carried on along the outcrop of the ore beds, and these old, abandoned trenches may be observed practically all the way from below Birmingham to Big Stone Gap, Va., in many places showing several parallel trenches where there were two or more beds of ore, or where one bed had been repeated by folding or faulting. In some places the ore beds were not more than one foot thick, and, of course, as soon as they were cut back to heavy cover, they were abandoned, and only the thicker beds were mined underground. Under present conditions an ore bed less than 2 feet thick cannot be mined profitably underground, and unless it is rich ore, it must be more than 2 feet thick in order to be considered.

The following six analyses [Table I] of Clinton ores, showing the potash content, have been made by the United States Geological Survey.

The writer has traced practically all these Clinton beds throughout the length of their outcrops in the four Southern States, and has been impressed with the great extent of the beds that fall just below the present workable grade either in thickness or in composition. Included in this classification are beds carrying shale

†Catlett, Charles. The blast furnace as a potash producer: *Manufacturers' Record*, May 11, 1916, pp. 41-42.

†Smith, Philip S. The gray iron ores of Talladega county, Ala. U. S. Geol. Survey Bul. 315, 1907, p. 177. (Cited from R. Crowell.)

intimately mixed with the hematite in the form of thin partings, lenses and minute concretions. Such ores are very difficult to free of shale, except by crushing finely and washing processes that are at present too costly. Another type of lean ore is that containing much free silica in the form of fine to coarse sand. This sand is often coated with hematite, and the ore containing it has also to be finely crushed and washed to effect a separation of the iron oxide and silica. Various experiments have been made, involving the use of heavy liquids and air separation methods, but none has proved commercially practicable. Therefore, if the potash content of these leaner ores proves to be uniformly higher than that of better-grade ores, and it proves possible economically to separate the potash salts, such as potassium cyanide, in the blast furnace gas, then the possibility of making use of these lean ores within the present generation seems far more encouraging than otherwise.

All these analyses show some potash, most of them only a small fraction of 1 per cent, it is true, but one of them, No. 6, shows 2.56 per cent. The first five samples represent hard to soft ores, containing little or no shale. Number 6 is typical of the lean, shaly ores

TABLE 1—ANALYSES OF CLINTON IRON ORES FROM ALABAMA AND TENNESSEE.

	1	2	3	4	5	6
Silica (SiO ₂)	5.00	7.92	7.62	7.63	7.56	27.67
Alumina (Al ₂ O ₃)	2.82	3.07	4.31	3.64	4.14	19.39
Iron (Fe)	27.22	37.32	52.55	50.79	37.87	29.51
Manganese (Mn)	.30	.33	.31	.58	.05	.03
Titanium dioxide (TiO ₂)	.11	.10	.12	.26	.41	.62
Lime (CaO)	24.84	13.77	.40	1.68	12.52	5.93
Magnesia (MgO)	1.63	1.71	.47	.50		
Phosphorus (P)	.43	.57	.53	.73	.31	.37
Sodium oxide (Na ₂ O)	.10	.10	.13	.12		
Potash (K ₂ O)	.22	.25	.30	.33	.17	2.56
Sulphur (S)	.05	.05	.02	.07		
Carbon dioxide (CO ₂)	19.89	12.29	.32	3.04		
Water (H ₂ O)	5.61	6.11	10.11	8.99		
1. Hard ore, Chamberlain, Tenn.						
2. Semi-hard ore, Chamberlain, Tenn.						
3. Soft ore, Chamberlain, Tenn.						
4. Soft ore, Chamberlain, Tenn.						
5. Hard ore, Greasy Cove, Ala.						
6. Lean, shaly, hard ore, Crudup, Ala.						

that have a wide extent in the Chattanooga region. Crushing and washing might reduce the silica and alumina appreciably, the potash slightly, and increase the iron content, but the process would be expensive, and no ore has yet been believed that it would pay. Here, then, is a problem for the blast-furnace chemist and metallurgist. If the potash in these shaly ores can be recovered, it should make available as an ore of iron a tonnage of material far in excess of the great total now already credited to the South.

The center of one of the shaly belts of Clinton ore is near Chattanooga, Tenn., and this city would be a logical place at which to try out the potash recovery process, in connection with one of the local blast furnaces. In the very middle of the Birmingham (Ala.) district are deposits of sandy ore about 16 feet thick, and there are large quantities of shaly ore adjacent to the city in West Red Mountain, and also in the north-east and southwest extremities of the district.

HINTS ON INSPECTING CANNED FOODS.*

By DR. W. D. BIGELOW,†

The examination of canned foods may be undertaken to assist in controlling the character and quality of the product; to establish its commercial value and grade; to fix the responsibility for defect in food or package; or in connection with the enforcement of food laws. Whatever the intimate object, the immediate purpose is to ascertain as exactly as possible the nature, character and quality of the product under examination.

This includes a knowledge of the raw product and method and conditions of manufacture.

In the examination of canned foods, the external appearance of the can should be carefully noted. If the can appears "flat" (i. e. if the ends are concave), it should be "knocked" with considerable force on one end on a substantial table or block of wood. If the lower end of the can does not remain concave the vacuum in the can is not as great as it should be. The temperature at which the can is examined must be considered in this connection.

A lot of cans may be springers in the summer and the ends concave the following fall and winter. They may be springers during a hot wave and "flat" in the same location the following week. The fact that a can does not have a good vacuum or even that it has bulged ends means nothing in itself, but may be significant when considered in connection with other data.

Cans whose ends bulge ever so slightly are not merchantable and their sale to consumers should not be permitted. Yet that condition does not usually mean decomposition when found in the retail trade. Very frequent and very serious errors have been made of assuming that all "swells," as they are popularly termed, are due to decomposition.

Spoilage rarely occurs with acid fruits unless the can be leaky. In this class of products the swelling of the can (in the absence of leaks) is almost invariably due to hydrogen set free by the action of the fruit acid on the metal of the container. The amount of hydrogen is influenced little by the method of canning or by conditions within the control of the packer.

The number of vent holes appearing in the can is a matter which has occasioned frequent error. No opinion can be formed of the character or history of canned foods by the number of vent holes in the can. The procedure which gives two vent holes is this. The cans are sealed, tipped and given a kettle exhaust; again vented to permit the escape of air, and the new vent hole then sealed for sterilization. It sometimes happens that the closing of the vent hole is prevented by solid material such as meat lying against it. When this occurs the can is vented in still another place, and

*Paper presented at recent Food Commissioners' Convention, Detroit, Mich.

†Chief Chemist of the National Canners' Association.

this is continued until a spot is found that is not in contact with the contents of the can. Even when the method just described is not employed, two or more vent holes are occasionally found in hole and cap cans containing foods of all descriptions.

With sanitary cans there are various reasons why a vent hole may be found. One not familiar with the industry might suspect reprocessing on seeing the cans here described. Presence of vent holes is never proof of decomposition.

On opening the can the odor, flavor and appearance of the contents should be carefully observed. The importance of establishing the true commercial grade is not always fully understood. A fancy or first quality article, for instance, can only be prepared from a raw product grown under proper conditions, harvested at the best stage of maturity and canned promptly. If the raw material is not of suitable grade an experienced man will recognize that fact by the appearance or flavor of the finished product. To retain a high quality they must be canned as soon as possible after they are harvested. A movement is under way to make the commercial grades more uniform and to have the products so labeled that these grades will be understood by the purchaser.

The importance of odor and taste in the inspection of canned foods cannot be overstated. The proper technique must be worked out with each product. If bacteria are recognized by size and shape their presence may be confirmed by bacteriological stains. If either yeasts or bacteria are found in considerable numbers the analyst should endeavor to find the reason for their presence. Obviously this method is not applicable to products made by process of fermentation; kraut, for instance.

The presence of bacteria in considerable numbers is merely an indication of the beginning of bacterial change at some time in the history of the product. It may be due to allowing a few cans to stand too long (because of a breakdown in the machine) after filling and before sterilizing, or to storing the raw product for a number of hours in boxes or baskets, as is done with fresh vegetables in our city markets. This method may help or mislead an analyst according to his ability and experience.

Experience with samples of known character, both fresh and canned, is absolutely necessary. Without such experience, the analyst can only be sure of making serious mistakes. It should be borne in mind that this is a microscopical and not a bacteriological method. It is used in determining the presence of dead microorganisms. It is, therefore, widely different from the bacteriological method.

In the examination of canned foods, a bacteriological examination is only of value when considered in connection with other methods of analysis. A food that has undergone bacteriological decomposition may be sterile because of the inhibiting action of products

on the life functions of the organisms causing the decomposition. On the other hand, it is believed by some that canned foods may contain aerobic bacteria which cannot develop because of the absence of oxygen and which may, therefore, remain dormant for a considerable time. The truth is that canned foods are almost universally sterile. At the same time bacteriological methods are of more value in research investigations relating to canned foods than in their inspection. In the case of goods very recently packed and to determine whether the process of the plant is sufficient, a bacteriological examination is of value when used in connection with the other methods described above.

Determination of acidity is a method with which relatively little has been done in the examination of canned foods. The laboratories that have used it have not tabulated their results and it is desirable that authentic data of this nature be secured. An abnormally high acidity or, under some circumstances, an abnormally low acidity may be of much value when considered in connection with the results of the other methods.

When the can is opened the fill should be carefully noted.

If the can be opened by cutting around the side, near the end, it is often convenient to pour the liquor through the opening thus made before turning back the top. It is important that in the examination of a single product a uniform method of separating the drained solids be employed.

It is often important for the analyst to consider the relation between the drained solids found in the can and the weight of food originally weighed into the can. In working with fruit packed in syrup, the specific gravity of the syrup may be determined. Then, taking into consideration the average sugar and water content of the fruit and the proportion of that fruit in the contents of the can the analyst can calculate approximately the weight of fruit and strength of syrup that was used originally. Whether the drained solids and liquor be weighed or not, a record should be made of whether the solid portion of the contents appears to be present in the right amount.

The analyst must bear in mind that the examination of one or two cans will often lead to incorrect conclusions. No matter how careful a packer may be, it frequently happens that the amount of brine in the can is either too much or too little. In a well managed corn cannery, for instance, there is always one man whose duty it is to open cans at frequent intervals to determine whether the corn is of the right consistency. The character of the corn changes from hour to hour, requiring that the relative amount of corn and brine shall be changed from time to time to give the proper result in the finished product.

Cans should be carefully examined to determine whether they are tight. This is more important in constructive work checking up the efficiency of a plant

than in the enforcement of food laws. It is just as essential for the canner to know when his cans are defective as when they are not completely sterilized. In both cases he may expect spoilage.

In the examination of the can as in the examination of the contents, it is obvious that the results obtained from a single can may be misleading. There are many reasons for this. For instance, small leaks, after admitting contaminated air or contaminated water from the cooling tank, may be closed by particles of food or, as in the case of water pipes, by rusting. After examining a half dozen cans, the writer frequently sends for a case and sometimes several cases. Even then an inspection of the entire lot in the storeroom will often throw additional light on the cause of the difficulty.

The nature of any further examination must depend on the particular variety of food and, to some extent, on the character of the sample and the reason for the examination. The causes should be understood of various discolorations that are sometimes found on the inside of the can and on the surface of the food.

Before opening a can of food it is often of value to determine the vacuum in the can by means of a suitable equipped gauge. This is a matter which has no significance in itself but may be of value when considered in connection with other data.

The amount of tin (or perhaps soluble tin) and iron in acid fruits may be significant when considered in connection with other data. On the other hand, with vegetables, such as asparagus, string beans and pumpkin, whose action on the tin is believed to be due to amino bodies, there is no relation between the amount of tin in the food and the amount of hydrogen in the gas content of the can. We are just beginning to understand this subject.

It may sometimes be of interest to determine the composition of the gas in a can with bulged ends. When the can is sealed the air is not entirely removed. The composition of the gas present, therefore, may sometimes serve to confirm data obtained by other methods of examination.

The American Commercial Attaché at Peking, China, reports that as a result of the war there has been a rapid development of the manufacture of potassium chlorate in Japan. An oversupply of the product has now affected the market. There are about 33 factories, and the total output is placed at 7,000 bbls. a month, which will be increased to 10,000 bbls. when extensions now projected are completed. The normal domestic consumption is about 7,000 bbls., but the demand is now below this figure, and prices have declined greatly. The Japan Weekly Chronicle says it seems not impossible that they may go down to a point where the less substantial manufacturers will have to close their plants. There has been a little temporary improvement, however, it states, as the result of a reported large order from Russia.

AN EXPLANATION OF THE FLOTATION PROCESS.*

By ARTHUR F. TAGGART** and FREDERICK E. REACH,†† NEW HAVEN, CONN.

INTRODUCTION.

The flotation process for the concentration of ores is a method by means of which one or more of the minerals in the ore (usually the valuable ones) are picked up by means of a liquid film and floated at the surface of a mass of fluid pulp. Here they are separated from the other minerals, which remain immersed in the body of the pulp. In general, the minerals which are floated are sulphides of metallic luster, but some other minerals of metallic luster such as graphite and some sulphides with adamantine luster, such as sphalerite and cinnabar, are amenable to treatment by the process.

The importance of flotation lies in the fact that it is primarily a "slimes process" by means of which the particles of valuable mineral, too fine for efficient gravity concentration, are saved with a high percentage of recovery. Recoveries in the mills treating low-grade copper sulphide ores have been advanced to 20 per cent, by the installation of the process and similar increased savings have been accomplished by the same means in mills treating sulphide ores of zinc and lead.

When finely ground ore containing sulphides mixed with a siliceous or earthy gangue is brought gently onto the surface of a body of water, in a direction forming an acute angle with the surface of the water, a considerable portion of the sulphide constituent of the ore floats on the surface of the liquid, while the gangue sinks. This is the so-called film flotation, exemplified by the Wood and Macquisten processes.

When gas bubbles are introduced into a fluid pulp composed of finely ground ore and water, to which has been added (1) a small amount of certain oils, or (2) a small amount of certain acids or acid salts, or (3) a small amount of certain alkalis or alkaline salts, or (4) a small amount of a mixture of oil with acid or alkali, the sulphide particles in the ore are brought to the surface on the gas bubbles. These collect in a froth heavily laden with sulphide particles. The gangue particles are not brought up by the bubbles, but remain in the mass of the pulp. This is the so-called froth flotation. Its variations, acid-froth, agitation-froth, and pneumatic-froth processes are discussed in detail later.

The points to be explained in the operation of these processes are: (1) The flotation of solid particles in a liquid the specific gravity of which is less than that of the solid; (2) the preferential flotation of the sulphide portion of the mass; (3) the functions of the reagents used.

*From Transactions American Institute of Mining Engineers. The paper is to be presented at the Arizona meeting of the Institute.

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THEORY.

The theory here presented in explanation of the points listed in the preceding paragraph appeals to the following physical phenomena: Surface tension, adsorption, adhesion and viscosity. The first three of these are closely related

Surface Tension.

Every liquid surface in contact with a gas or its vapor, behave as if it were under tension. The value of this contractile force per unit width can be measured. Its value for water, 74 dynes per centimeter, is higher than for any other well-known liquid. (Liquid metals and fused salts are of course excepted.) This fictive tension is a convenient conception for many discussions and may be explained in terms of the intermolecular attractions of the sub-

whose surface tensions are T_1 and T_2 respectively were brought together, the work due to the molecular attractions would be $(T_1 + T_2) \cdot A = W$, provided there was complete union, but if there is not complete union, there will be an interfacial tension T_{12} , and the energy equation becomes

$$(T_1 + T_2) \cdot A - T_{12} \cdot A = W$$

or

$$T_{12} = T_1 + T_2 - \frac{W}{A}$$

i. e., the interfacial tension T_{12} is the excess of the sum of the two tensions over the work which is done by them in allowing a unit area of the two liquids to come into contact. If a liquid is brought into contact with a solid, the energy equation is

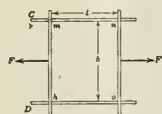


Fig. 1.

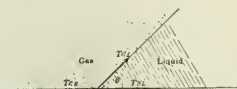


Fig. 2.

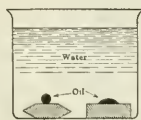


Fig. 3.

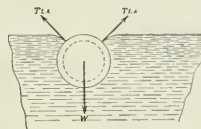


Fig. 4.

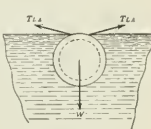


Fig. 5.

stances forming the boundary. Another and very useful way of considering the phenomenon is to regard each unit of surface as having associated with it an amount of potential energy which is numerically equal to the surface tension. This relation is established as follows:

If two wires, A and B (Fig. 1), are so placed as to slide on two fixed wires, C and D , and if the wires, A and B , having been in contact, are separated a distance l against the pull of one of the surfaces only of a film, $mnoh$, by applying the force F , the work per unit area will be

$$\frac{W}{A} = \frac{Fl}{lb} = \frac{F}{b} = T$$

which is obviously equal, numerically, to the force per unit width or the surface tension, T , of the one surface considered. Applying this conception of surface energy to different cases of contact, we can develop some statements of the relations of forces which are important in explaining many of the phenomena observed in flotation.

Consider first that two blocks of liquid, which have become rigid without any change in their other properties, are drawn together by the mutual action of their forces of molecular attraction until they perfectly unite over an area A . They would do an amount of work that we will represent by the letter W . Now consider that the same two bodies when brought near together, but not into contact, become liquid and unite over the area A . The work done is again W , but in this case it can be considered as due to the shrinkage of the surface by an amount $2A$, whence $2AT = W = A(T + T)$, where T is the surface tension of the liquid. If two different liquids

(gas or vapor effects being excluded), where TL = the surface tension of the liquid,

W_1 = the work done in bringing a unit area of the liquid and solid into contact, and TL_s = the interfacial tension.

If, therefore, $W_1 = TL$, the solid has the same attraction for the molecules of the liquid as the molecules of the liquid have for each other and there will be no interfacial tension. If $TL > W_1$ the interfacial tension TL_s will be positive; if $TL < W_1$ there will be negative interfacial tension or a surface pressure. In the latter case the liquid will tend to spread over the solid.

Angle of Contact.

When, as is the common case in the flotation process, there are three substances in contact, a system of forces as shown in Fig. 2 is brought into play. If O does not move indefinitely to the right or to the left, equilibrium will be attained when

$$T_{SL} = T_{GS} \times T_{GL} \cos \theta$$

or

$$\cos \theta = \frac{T_{SL} - T_{GS}}{T_{GL}}$$

where T_{GS} , T_{GL} , and T_{SL} are the interfacial tensions or pressures at the gas-solid, gas-liquid, and solid-liquid contacts respectively. From this equation is deduced the important conclusion that as T_{SL} increases with respect to T_{GS} , the angle of contact θ becomes smaller (the gas and liquid being the same), or, in other words, the angle of contact is a measure of the tendency of one fluid to replace another on the surface of a solid. We have examined the angles of contact of the water-air, oil-air, and oil-water sur-

faces against a number of the common minerals. We have found, in general, that the air-water contact angle is less for gangue minerals than for sulphide minerals; that the air-oil contact angle is less for sulphides than for gangues and less for any given sulphide than the air-water contact angle; and that the water-oil contact with solids takes the form shown in Fig. 3.

We found further that the invariable effect of oiling a solid surface is to reduce the air-water contact angle. This latter phenomenon is undoubtedly aided by the reduction of the surface tension of the water due to contamination by the oil. This is further discussed later.

The conclusions forced by observation of the above phenomenon are:

1. That water has a smaller tendency to displace air on the surface of sulphide minerals than on the surface of gangue minerals.
2. That the tendency of oil to displace air is greater at the surface of sulphide minerals than at the surface of gangue minerals.
3. That oil tends to displace water on the surface of sulphides and that water tends to displace oil at the surface of gangue minerals.
4. That water displaces air more readily on an oiled solid surface than on a clean surface of the same solid.
5. That these tendencies toward displacement are due to the interfacial tensions or pressures existing between the various substances, and that the resulting action of these interfacial forces is a manifestation of the tendency toward reduction of the total potential energy of the system. Wherever an increase in the solid-fluid interface will decrease the potential energy, such a change will occur.

These conclusions suggested the following confirmatory experiment.

A ring, 6.17 cm. outside diameter and specific gravity of 1.38, made of aluminum tubing, 0.63 cm. diameter, was cleaned and floated without trouble on the surface of pure water. The shape of the water surface at the air-water contact is shown in Fig. 4. The ring was then oiled slightly. The air-water contact angle was reduced, as shown in Fig. 5, to such an extent that it was impossible to float the ring. The same was true, as might be expected, when a cylinder of aluminum replaced the ring. A similar cylinder of glass tubing exhibited such a small air-water contact angle that it could not be floated.

Adsorption.

The surface layer between two physical phases is the seat of conditions of density and viscosity, also of apparent forces or energy manifestations, which are notably different from those in the bulk of either phase. On philosophical grounds it is impossible to consider that a real physical discontinuity occurs at the boundary between two media. In other words, there must be a very thin layer of transition in which

there is a rapid but continuous change in the concentration of the components. This change in the concentration of a component at the interface is called adsorption, and may occur even between two phases which are ordinarily regarded as immiscible.

Adsorption at a gas-liquid interface may be demonstrated as follows: If a solid, which has been heated in a vacuum, is introduced into a measured volume of a gas over mercury in a calibrated tube, an amount of the gas will be adsorbed, as is shown by the change in pressure and volume compared to the space originally occupied.¹ These additional facts are established:

- (a) The amount of the gas adsorbed at constant temperature increases with the pressure.
- (b) It is different for different gases.
- (c) It is different for different solids.
- (d) It increases as the temperature decreases.
- (e) There is an energy transformation which is indicated by the heat developed through adsorption, analogous to the Pouillet phenomena mentioned later.
- (f) Chemical reactions are assisted by the adsorbed layer.

It follows that the gas layers must vary in density, falling off rapidly with increasing distance from the solid. Quincke assumes that the density of the gas next to the solid is equal to that of the solid and concludes that the amount adsorbed will increase with the density of the solid. From these facts we conclude:

1. That gases and solids exhibit selective adhesion and that, therefore, gas bubbles will attach themselves more persistently to some substances than to others.
2. That this selective adhesion is a manifestation of a definite amount of energy possessed by each unit area of a gas-solid contact, and that this potential energy is capable of variation.
3. That chemical reactions which diminish this potential energy are aided by adsorption.

Adsorption at a liquid-solid surface manifests itself in a vacuum, or where the vapor phase is negligible, by the way in which the liquid spreads or gathers itself together on the solid; in other words, in the way in which the liquid wets or adheres to the solid. It is further manifested by an evolution of heat, known as the Pouillet phenomenon. A calculation of the condensation necessary to evolve this amount of heat, in the case of water against glass, indicates that the specific gravity of water in the adsorbed layer is increased to about 2.1.²

Adsorption of the gas at a gas-liquid surface is indicated

1. By the effect on the surface tension. The surface tension of a freshly formed mercury surface does not change in a vacuum, but falls off in the presence of different gases for about an hour. Certainly the

¹Freundlich: *Kapillar Chemie*, p. 92.

²Lewis: *Phil. Mag.*, 20, p. 502, 1910.

density of a liquid cannot be constant at the boundary but must go over continuously into that of the gas.

2. By the increase in the solvent power of the surface.³

3. In the case of contaminated liquids, by the concentration of one or more of the components of the liquid at the gas-liquid surface. Every unit area of such a boundary possesses a definite potential energy which always tends to a minimum. If, therefore, the surface tension of a solution depends upon the presence of any component, such a change of concentration of that component will occur as will reduce the potential energy, *i. e.*, the interfacial tension. In other words, any component which reduces surface

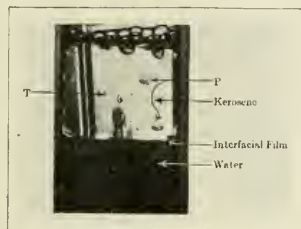


Fig. 6.

tension will be found in excess at the surface of a solution. For example, the surface tension of water is greater than that of alcohol. Experimentally, a drop of alcohol on a thin film of water rapidly reduces the surface tension of the water and the latter draws away from the alcohol. On the contrary, a drop of water on a thin film of alcohol spread over glass does not at once diffuse into the film but remains gathered in a heap. Such diffusion would increase the surface energy of the system, hence the water concentrates away from the gas-liquid surface. The greater viscosity of the surface of a solution above that of the bulk, or of that of a pure liquid, has long been recognized⁴ by its damping effect upon a swinging magnetic needle and may properly be ascribed to gas-liquid adsorption. Closely connected with this is the formation of elastic solid skins or very viscous layers at a free surface, as, for example, in the case of solutions of peptone and dye stuffs. A peculiarity of saponine solution is the rigidity of its surface while the interior remains more mobile.⁵ The surface of a freshly formed fairly concentrated solution of fuchsin is quite mobile, but in the course of a few hours it changes to a reflecting skin with solid properties. Similar results are obtained with methyl-violet and peptone. In the case of the latter substance the skin is highly elastic. There seems to be no doubt that true adsorption is present here. In the case of crystal-violet, which closely resembles methyl-violet in its properties, a solution of 1 g. to the liter lowers the surface tension from 75 to 69.9 dynes per centi-

meter. Other causes for the production of a solid layer may, however, be present, for many of these substances in concentrated solutions stiffen into gels and since the concentration of the contaminant is great at the surface and the solubility has also a different value, the solid remains persistently. Either a chemically irreversible change or a transformation into a more difficult soluble phase at the surface is clearly the explanation of the persistence of the froth in albumen solution and the like. The properties of such surfaces apparently pass over imperceptibly into those of colloids.

Adsorption at the boundary between two liquids is evidenced by the effect on the interfacial tension just as in the gas-liquid solution surface, although the process is not one usually described as ordinary solution and one may also have to reckon with chemical reactions in the transition layer. With liquid-liquid surfaces, as in gas-liquid surfaces, the adsorption frequently gives rise to very viscous layers. The presence of such a viscous layer at an oil-water interface is easily shown by pouring any clear oil, kerosene, liquid vaseline, etc., onto water and then bubbling a gas through the water. Such an experiment is shown in Fig. 6. The interface has all the appearance of an elastic skin. Bubbles rising through the water and striking the under side of the interface stretch the film (see H, Fig. 7), and rising farther drag away a mass of water surrounded by this viscous layer. The system now appears as shown at M and rises to the oil-air surface on account of its lower specific gravity. Here the film, together with the excess water carried

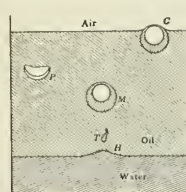


Fig. 7.

up as shown at C, breaks away and falls back through the oil, not in spherical form, as would be the case were the water drop not surrounded by a viscous film, but in hemispherical form (see P, Figs. 6 and 7) often trailing behind it a film with ragged edges, as it broke from the bubble. The tadpole-shaped water drops, T, (Figs. 6 and 7) are further evidence of the high viscosity of the oil-water interfacial film.

Viscosity.

A marked increase in the viscosity of interfacial films is produced by the presence of finely divided solid matter. This increase is apparent in the experiment just described when finely powdered sulphide is thrown into the oil and allowed to settle to the interface, where it becomes entangled in the film. When gas bubbles are introduced, as before, the return water

³Pockels: *Nature*, Mar. 12, 1891, p. 439.

⁴Daniells: *Physics*, p. 258, Fr. p. 76.

⁵Boys: *Soap Bubbles*, p. 115.

drops, coated with a film containing the solid particles, are much more irregular in shape than previously, and their coalescence after reaching the interface requires days or weeks. An even more convincing proof of the increase in viscosity of an interfacial film is given by the following experiment. If a needle is floated at the center of a surface of pure water in a beaker 4 in. in diameter and a chip of wood is floated near the wall of the beaker, the needle may be caused to revolve by means of a magnet without disturbing the chip. If the surface of the water is dusted over with fine ore, the whole surface together with the chip moves as though it were a rigid solid.

SUMMARY.

The potential energy at a gas-sulphide contact is less than at a gas-gangue contact; hence gas bubbles will cling with greater persistence to sulphides than to gangues.

Oil replaces water at the surface of sulphide minerals.

Water replaces oil at the surface of gangue minerals.

Water replaces gas more readily at an oiled surface of a solid than at a clean surface.

The addition of any contaminant to water lowers the surface tension.

In any body of contaminated water there will be a concentration of the contaminant at the air-liquid surface.

Adsorption at a gas-liquid surface lowers the surface tension and increases the viscosity.

Adsorption at a liquid-liquid surface produces a film whose viscosity is higher than that of the bulk of either liquid.

The presence of finely divided solid matter in a film markedly increases the viscosity of the film.

APPLICATION TO COMMERCIAL FLOTATION PROCESSES.

Film Flotation.

Pulp with or without oil or acid is fed gently, at an acute angle, onto the surface of a body of still water. The sulphide floats and the gangue sinks.

Possible cases:

Case 1.—Sulphide, gangue, water.

Case 2.—Sulphide, gangue, water, oil.

Case 3.—Sulphide, gangue, water, acid.

Case 4.—Sulphide, gangue, water, acid and oil.

Case 1. Sulphide, Gangue, Water.—The governing factor in the initial flotation of the sulphide and immersion of the gangue is the difference in the air-water contact angle with the sulphide and gangue surfaces respectively. If the difference is great, as in the case with galena and quartz, good separation is obtained. After a considerable amount of sulphide has been floated, if the surface flow is sufficiently impeded, the particles congregate into clumps by the well known phenomenon of apparent attraction of floating particles,⁹ a scum is formed (whose viscosity and re-

sistance to rupture are many times greater than that of the original water surface) and the floated particles are rendered more immune to immersion.

Case 2. Sulphide, Gangue, Water and Oil.—When oil is added in this process the phenomena are entirely different from the simple film flotation of Case 1. The oil concentrates at the surface since such concentration reduces the surface energy of the system. This adsorption of the oil at the gas-water surfaces causes the formation of a viscous film. When the mixture of sulphide and gangue is introduced at the surface, the sulphide particles tend to migrate into this layer and the gangue particles migrate into the water, for a sulphide particle in contact with oil represents the condition of least potential energy which is possible for the sulphide particle to assume in the system of oil, sulphide, and water. Likewise the gangue particle surrounded wholly by water represents the condition of least potential energy for the gangue particle to assume in this system. In this case also, the formation of a scum of floated sulphide increases the stability of the float.

Case 3. Sulphide, Gangue, Water and Acid.—The effects of acid are: (a) to diminish the surface tension of the liquid, (b) to diminish the gas-liquid contact angle, and (c) to increase the viscosity of the gas-liquid surface. The diminutions of (a) and (b) are more marked with gangue minerals than with sulphides. The result is that cleaner concentrate may be expected than in either of the previous cases, but at the expense of richer tailing.

Case 4.—Sulphide, Gangue, Water, Oil and Acid.—In this case a combination of results such as can be predicted from the preceding cases is obtained.

Froth Flotation.

In order to explain froth flotation it is necessary and sufficient that the gas of each bubble shall be enclosed by a film of contaminated water which shall possess the following characteristics:

1. Low surface tension.
2. High viscosity.
3. A variable concentration of the contaminant (reagent).
4. A preferential adhesion of the bubble film to the sulphide mineral compared to that for the gangue minerals.

We will examine first the conditions required for the formation of a froth, or the continued existence of a thin film. Solutions which form froth are pre-eminently aqueous solutions and the properties of the liquid film are only secondarily determined by those of the gas.

The durability of a liquid film depends upon one or more of the following conditions:

1. A low surface tension which is locally variable so as to produce stable equilibrium.
2. High viscosity, which may pass over into
3. Chemical irreversibility and the production of solid skins.

⁹Hastings and Beach: General Physics, p. 156.

Pure liquids do not foam; for example, water alcohol. The reason is obvious. As the film is thinned out by stretching or by draining away of the liquid, the surface tension is reduced at some part below the general constant value. As soon as this begins the thicker and more powerful parts of the film drag away from the weakened parts which at once completes the rupture. These inequalities evidently would not be so marked or rapid in their operation if the surface tension were low. Increase of viscosity would also slow up the process. High viscosity and low surface tension do not occur in pure liquids. But the most important condition for durability is some means by which the equilibrium of the forces at any point in a film may be restored, when a variation of some of the forces occurs. In the case of a compound liquid or solution this is effected by the adsorption or change of concentration of one or more of the components in the film.

The surface tension of a solution is in general notably different from that of the pure solvent, and in case of water, whose surface tension is the greatest of any liquid with which we are concerned, even a minute trace of impurity is sufficient to lessen its surface tension considerably.

Consider a film of water stretched on a vertical ring of wire. If the surface tension remained constant, as it does in the pure liquid when the thickness exceeds 0.000001 cm., the weight of the lower part would stretch down the upper part until it broke. If the water contains some component whose depletion at the weaker points increases the surface tension, equilibrium will be preserved. In the stretching of a film, and in the general running away of the liquid between the surfaces of the film, which reduces the total available amount of the contaminant, such decrease of the concentration and increase of surface tension does occur, and the film remains stable under a considerable variation of external conditions. The formation of bubbles as a result of this variation of surface tension alone is well exemplified by a simple aqueous solution of soap or of acetic acid. The running out of the liquid between the two surfaces is greatly retarded by the viscosity of the liquid, a property which may be largely influenced by the surface adsorption of one or more of the components.

When, then, gas bubbles are introduced into a liquid pulp where oil is present there is formed about each bubble a liquid film whose surface tension is less and whose viscosity is greater than that of the bulk of the liquid. Some of the solid particles of the pulp move into the film and are raised to the surface with the bubble. Since there is a concentration of oil in the film, and since the diminution in potential energy at an oil-sulphide contact is greater than at a water-sulphide contact, the contaminated layer replaces the water on the sulphide surface and the sulphide moves into the bubble film, while the gangue, on which water displaces oil, remains in greater measure in the body

of the pulp. The bubbles, therefore, as they arrive at the surface, carry an excess of the sulphide minerals. Upon their arrival at the surface the bubble of the contaminated liquid persists, owing: (1) to their lower surface tension; (2) to their ability to adjust this tension to a state of stable equilibrium; and (3) to their greater viscosity which is markedly increased by the presence of the solid particles.

Mechanical-Agitation Froth Process.

Sulphide and gangue minerals are beaten up with water and oil, with or without acid, then allowed to flow into a box containing a considerable body of liquid nearly at rest. Bubbles coated with a preponderance of sulphide particles float to the surface and form a heavy, persistent froth. The gangue particles sink.

Two cases arise:

Case 1.—Sulphide, gangue, water and oil.

Case 2.—Sulphide, gangue, water, oil and acid.

Case 1. Sulphide, Gangue, Water and Oil.—When this pulp is beaten, air is mechanically entrapped in the form of bubbles. At the surface of every bubble in the mass there is a gas-contaminated-liquid contact which results in the adsorption at this surface of the contaminant oil, and the production of a viscous film into which the sulphide particles, circulating in the mass, pass with a diminution in the potential energy of the system. The result is that in a very short time after the air bubble is entangled in the pulp, it is surrounded by a viscous sheath composed of an oil-water interfacial film in which are entangled a large number of sulphide particles. The presence of the solid particles greatly increases the viscosity of the bubble sheath. When the solid-coated bubble arrives in the settling box of spitzkasten it rises to the surface. Here the bubble persists, or, bursting, transfers its load to other bubbles. This bubble persistence is due to a combination of several factors. The oils used have, in general, a slower evaporation rate than water. The tension of the bubble film is lower than the tension of a pure water bubble. The bubble has the power of adjusting itself to its tension, within limits, without bursting. The presence of the large amount of solid matter enormously increases the viscosity of the film.

Case 2. Sulphide, Gangue, Water, Oil and Acid.

—The addition of acid has the twofold effect of further lowering the surface tension and increasing the oil-solid

adhesion ratio ———. The result is, in general, water-solid cleaner concentrate with or without an increase in the sulphide content of the tailing.

Heating the pulp has, in some cases, a beneficial effect. Where this is true it is probably due to (a) decreased surface tension and consequent increased stability of the froth; (b) increased number of air bubbles formed by the air released from solution; (c) in the case of viscous oils, the greater area over which

oil is spread and consequently the greater number of bubbles with a viscous oil-water interfacial film; (d) probable increase in solubility of the oil and consequent greater diffusion, resulting in more widespread adsorption in bubble films.

Pneumatic Froth Process.

Sulphide and gangue minerals mixed with water and oil, with or without acid, are run into a tank with a porous bottom through which air is forced. The air bubbles rise to the surface with a coating of solid particles, preponderantly sulphide, while the gangue particles sink.

The principles involved in this method are the same as explained in the agitation-froth process. The only difference is in the method of introducing air. The result of this difference is that the bubbles in the pulp are much larger than in the agitation froth method; they arrive at the surface less heavily loaded in proportion to their area; the bubble films are, therefore, less viscous, and the froth less persistent.

Potter-Delprat Process.

Sulphides and carbonates, with or without other gangue minerals, are treated with hot, dilute sulphuric acid. Bubbles of carbon dioxide and hydrogen sulphide are formed which rise to the surface with a sulphide coating and there form a froth. That part of the gangue not dissolved remains immersed. In this method as in the other froth methods, gas bubbles are formed which are surrounded by films of contaminated water, the contaminants in this case being sulphuric acid, lead sulphate, calcium sulphate and other salts formed by the action of the sulphuric acid. The films have a higher viscosity and a lower surface tension than is possessed by the bulk of the liquid. The sulphides move into the bubble films because the system composed of sulphide and this contaminated layer has a lower potential energy than the system composed of the pulp in the bulk of the liquid. The writers at first suspected that the selective action in this case might be due to preferential gas adsorption at the gas-sulphide contact, as opposed to a gas-gangue contact, but microscopic examination of mineral froths collected from the process showed that the solid particles in the froth were completely within the films and at no point in contact with gas. The persistence of the froth is due to the factors explained in connection with the other froth processes.

While the writers have made no appeal to electrostatic forces or to colloidal phenomena in this discussion, they realize that the potential energy existing at the contact of dissimilar substances may well include electrical forces and that migration of the suspended solid particles under the influence of electrical charges, similar to the migration of colloids, may account for some of the selective action of the bubble films. But the agitation of the pulp in the mechanical and pneumatic-froth processes and the generation of carbon dioxide gas on carbonate particles in intimate contact with sulphides in the acid-froth process, are sufficient,

in their opinion, to bring every sulphide particle into contact with a bubble film. Once in contact, the preferential adhesion of the contaminated layer to a sulphide surface in the presence of water is sufficient to account for the persistent attachment of the sulphides to the bubble films, while on the other hand, the replacement of gas or oil by water on the surface of gangue particles explains the wetting and continued immersion of the latter.

The writers have a considerable bulk of experimental data on which many of the statements in the foregoing explanation are based. These, together with the data from other experiments which are projected, and photographs of many of the phenomena mentioned, they hope to present in a later paper.

Manufacture of Quebracho Extract in Paraguay.

A representative of American capitalists has applied to the Congress of Paraguay for a concession for the erection of a factory at Asuncion for the manufacture of Quebracho extract. The concessionaire proposes to produce at least 15,000 tons of extract per year. He asks readjustment of the export duties on extract of quebracho. It is asked that the present fixed rate of export duty on extract of quebracho, 10 gold pesos (\$9.65) per ton (2,240 pounds), be abolished and an export duty of 1 gold peso (96.5c) per ton be established on extract of quebracho when the market value of this commodity does not exceed 100 gold pesos (\$96.50) per ton. The quotations of extract of quebracho on the bourse of Buenos Aires, shall determine the market price for the purposes of levying export duty. When the market price of extract of quebracho exceeds 100 gold pesos per ton an ad valorem duty of 4 per cent shall be paid on the value exceeding the 100 pesos per ton, in addition to the 1 peso per ton to be paid on the first 100 pesos market value. In addition to this, concessionaire asks for exemption from import duties of machinery and other materials to be used in the construction and operation of the plant and exemption from fiscal imposts. In consideration for the granting of the concession, the concessionaire agree to advance the sum of 500,000 gold pesos, (\$482,500) as a loan to the Paraguayan Government. This loan is to bear interest at the rate of 5 per cent per annum and the amortization thereof shall be effected from the export duties that shall be due the Paraguayan Government for quebracho extract exported by the plant. The loan is to be made on the date of the signing of the concession and the amortization of the debt is to begin on the day set in the concession for the plant to commence operation—Jan. 1, 1918.

Chile's production and exportation of nitrate during July were both on a large scale. There were produced in all the oficinas 5,312,776 Spanish quintals (of 101.4 lbs. each) and the exports amounted to 5,674,088 quintals.

THE GRONWALL-DIXON ELECTRIC FURNACE.*

There has been in successful operation in Detroit for over a year an electric steel furnace with which the electric steel industry of the United States as a whole is but little acquainted. It is now known as the Grönwall-Dixon electric melting and refining furnace, and is operated by the John A. Crowley Company of New York and Detroit.

ORIGIN OF THE FURNACE.

When first introduced in this country, it was called the Grönwall furnace, but because of certain American patents secured by Joseph L. Dixon of the John A. Crowley Company the name was recently changed. While the Detroit installation is the only one commercially operating at present in this country, sales of several others have been arranged, and there were twelve in England and two in other countries operating or contracted for on January 1, 1916, according to the review of the electrical steel industry published in *The Iron Age* of January 6, 1916. But in Europe the furnace has been more familiarly known as the Electro-Metals furnace, as put out by the Electro-Metals Company, Ltd., of London, with which Mr. Dixon, a metallurgist and electrical engineer, was once associated. Essentially, however, the furnace is of Swedish invention.

Early in 1915 John A. Crowley, president of the company, returned from England after having concluded negotiations for the representation of the furnace in the United States and Canada. At that time it was better known here in connection with the ore smelting furnace of the same name used in smelting Swedish ores in Sweden. After careful investigation of a location arising from a decision to operate the furnace commercially in this country producing high-grade alloy and carbon steels, Detroit was selected. That city was regarded as offering the double advantage of a good market for the product of the furnace and a source of desirable and varied scrap.

Arrangements were concluded with the Railway Steel Spring Company, whereby at one end of its plant a 5-ton furnace was installed, with a provision that the billets of various steels be rolled into finished shapes by the same company. The first heat was taken out July 25, 1915, since which time there has been almost uninterrupted successful operation. On Aug. 18, 842 heats had been poured and incorporated into various sizes of billets.

The furnace at Detroit is cylindrical in shape. It is tilted by the usual worm-driven connecting rods operated by a motor drive through a reversing controller. The silica brick roof is constructed in a supporting steel ring made in halves, and is removable and replaceable by a spare one. Such a roof, it is stated, is capable of lasting 75 or more heats, but is usually replaced every two weeks. The assertion that

a roof so constructed is weakened by the four holes for the electrodes is not borne out by experience, as after more than 50 heats it easily withstood the weight of two or three men.

THE ELECTRICAL ARRANGEMENTS.

The furnace has two doors, front and back, the front being a combination pouring and charging door by using a removable spout. The use of two doors instead of three is considered an advantage. The electrodes are carried by an overhead support of beams, their weight being counterbalanced with a mechanical gearing for the control attached. An individual motor for each electrode operates this control, and they are energized through a system of contractors, located on the switchboard. The amount of current to be passed through each electrode can be set at a number of different steps by the operator, the current being so maintained by an automatic control. Indicating instruments for current and voltage in each electrode are also under the immediate observation of the operator. The operation of one to four furnaces can be readily watched by one melter and his assistant by locating all the levers for operating the switches on one panel.

This furnace differs from most of those operating at present in the United States, in that it uses two-phase current and four electrodes through the roof with a neutral one in the hearth. Though operating on a two-phase system, a three-phase supply is taken through two banks of transformers and changed to two-phase by a modified Scott three-phase to two-phase connection. Four vertical electrodes pass through the roof in furnaces of five or more tons capacity. In smaller ones, two such electrodes are recommended. The bottom electrode, which is of carbon and not of metal nor water-cooled, is protected from the molten metal by being imbedded under the hearth's lining.

The transformers are arranged so as to deliver a current of variable voltage. Each phase of the two-phase current is carried to a pair of the vertical electrodes, the bottom one being joined to the neutral point of the transformers, and hence called the neutral electrode. The two-phase current takes a perfectly balanced load from the three-phase supply mains.

The principal advantages claimed for the Grönwall-Dixon furnaces are:

Ease with which a large power input can be used in melting down cold charges.

The facility with which the melted metal can be agitated when refining by the influence of the neutral electrode in creating a magnetic movement of the bath, insuring more complete mixing.

The arcs can be thrown in series by means of a special arrangement of switches, in which case the bottom electrode carries the unbalanced load; or when thrown in parallel the bottom electrode serves as a common return. Operation can also be conducted in

*From *The Iron Age*.

several intermediate positions between series and parallel. For this arrangement it is urged that when melting on a cold charge or bottom when the resistance is high, rapidity of operation can be secured with the added economical advantage that large power input through a long arc of high voltage can be used without a waste of energy by passing large currents through the bottom.

Later this voltage can be reduced when refining, recarburizing, etc., by shortening the arc and thus decreasing decidedly the reflected heat on the walls and roof, which, of course, lowers the cost per ton of metal. Either the parallel or one of the modified connections is used with the short arc, the current passing through the bath to the bottom electrode; thus the proportion used is capable of being varied to almost any extent. This electrical system affords power companies a desirable load, effecting a transformer efficiency of over 98 per cent, with the service mains and power station undisturbed by any serious surges, the minor ones that take place during melting being absorbed by the interlocking of the phases by the transformers. The power factor is reported as 90 to 95 per cent.

THE GRADES OF STEEL MADE.

All grades of scrap are used—from high sulphur and phosphorus bolts, nuts and plate to nickel and alloy steel turnings. The furnace operates basic and is continuous. The more than 900 heats already made have included high and low carbon nickel steels, chrome-nickel steels, chrome-vanadium steels and high silicon and high manganese steels as well as any grade of plain carbon steel.

The high and low carbon nickel steels average 3 to 3.50 per cent in nickel. The high and low carbon nickel-chrome steels have contained 0.25 to 0.35 per cent carbon for the low and 0.50 to 0.60 per cent carbon for the high, with the nickel about 1.50 per cent and the chromium about 0.75 to 1 per cent. The low carbon steels have been especially employed for case-hardening. The chrome-vanadium steels have been made to contain on the average about 1 per cent chromium and 0.18 per cent vanadium. Special variations from these have been supplied. Most of these steels are being consumed by automobile and aeroplane builders.

Each heat is reported to average from 4 to 5 hr., with an energy consumption of 550 to 600 kw.-hr. per ton. Three hours is reported as the minimum under favorable conditions for some heats, averaging under 0.02 per cent sulphur and phosphorus with a consumption of only 460 kw.-hr. per ton.

Most of the heats made have been to a carbon specification of 0.35 to 0.65 per cent carbon. This necessitates recarburizing, as well as the addition when required of the ferroalloys. The company has its own chemical laboratory, and it is the regular practice to hold special alloy heats until a satisfactory in-

dication of the composition is obtained from the chemists so as to meet the exacting specifications.

TREATING MANGANESE SCRAP AND CUPOLA METAL.

The advantage of the electric furnace in general and this one in particular was recently demonstrated by several very interesting experimental heats made for a company interested in reclaiming its high manganese steel scrap. The scrap, which showed a manganese content of 12 to 13 per cent, was charged alone into the furnace. After complete melting, samples revealed the fact that the average manganese loss was slightly less than 0.75 per cent, which is decidedly less than the company had ever been able to secure by any other furnace or process.

Still another interesting experiment carried out at Detroit, and which is regarded as suggesting a field for such a furnace, is the electric refining of cupola metal. Encouraging results were achieved somewhat as follows:

Fluid cupola metal of the following analysis was charged into the Grönwall-Dixon furnace:

	Pct.		Pct.
Carbon, combined.....	0.63	Manganese	0.73
Carbon, graphitic.....	2.65	Phosphorus	0.313
Silicon	1.980	Sulphur	0.044

The metal was refined in the usual way and from it a 1-in. square test bar was cast. Physical tests of this bar were as follows:

Supported on knife edges 12-in. apart, it sustained a load, applied in the middle, of 3,050 lb. before breaking, the deflection being 0.215 in. The tensile strength was 27,570 lbs. per sq. in. and the Brinell hardness 202.

This experiment is reported as a sample of many excellent ones. While thus far it has been only experimental, it is believed by the company that the commercial field is wide.

COST OF THE STEEL.

The cost of producing a ton of liquid alloy steel or steel castings, refined to 0.025 per cent or under of phosphorus and sulphur, based on a year's operation of this 5-ton furnace, is given as follows:

	Liquid alloy steel.	Steel castings.
Electric energy, 550 kw.-hr., at 8c.....	\$ 4.40	(500 kw.-hr.) \$4.00
Electrodes, 20 lb., at 5½¢ per lb.....	1.10	1.10
Refractories	0.40	0.40
Alloys	0.61	0.61
Slag mixture:		
60 lbs. lime per ton of steel.....	0.25	0.35
6 lbs. fluor spar per ton of steel.....		
10 lbs. of coal per ton of steel.....		
Scrap and iron.....	14.00	12.00
Skilled labor	0.70	0.60
Unskilled labor	0.30	0.12
Total	\$21.76	\$19.18

About 5 lbs. of standard ferromanganese per ton of steel are found to be necessary to raise the steel from a minimum of 0.30 to 0.40 per cent manganese to the desired content. About 6 lb. of 50 per cent ferrosilicon per ton of steel are added to bring the steel to 0.15 per cent silicon. The estimated cost is 43¢ for the manganese and 18¢ for the silicon. Special alloys for special steel are extra.

The cost figures are based on the making of high-grade alloy steels to meet severe specifications, and it is emphasized that in producing steel castings these costs can be decidedly reduced because of no necessity to analyze the metal before tapping.

The experience of the operations thus far has demonstrated that it is unnecessary to use any deoxidizing agents, such as ferromanganese or ferrosilicon, except such as needed to meet specifications. It has been possible to add most of the desired alloys as scrap, or as soon as the charge was melted, and in some cases no manganese or silicon was at all necessary, demonstrating the non-oxidizing nature of the furnace operations. Absolute uniformity is reported as characterizing all steels made.

THE LIFE OF THE BOTTOM.

The duration of the original basic bottom is pointed to as noteworthy. It is still intact and in good condition after nearly thirteen months of constant use. This is attributed to the influence of the passage of the current through the hearth.

All ingots are bottom poured and weigh about 400 lbs. each. There has been very little evidence of segregation even in piped ingots, and there has been no difficulty in refining down to 0.01 per cent sulphur from an initial content of 0.10 per cent. These results are ascribed in part to the effect of the bottom electrode, which causes the current to pass through the metal, overcoming a tendency of the arcs to skim over the surface and causing an unusually high temperature. The same influence is claimed to have been responsible for the fact that there have thus far been no cold rings nor chilled bottoms in the furnace.

An interesting set of investigations is being conducted at present by the Detroit Edison Company of Detroit on certain electrical phenomena and other conditions arising from the application of electric current to such operations. In addition some special heats are being made of ferro-carbon-titanium-treated steel for incorporation in boiler tubes for use by the same company. The metallurgical phase of this is being investigated by the metallurgical department of the University of Michigan under Professor White.

The John A. Crowley Company has already completed plans for building a new plant of its own, situated in the western section of Detroit. It will have a 10-ton Grönwall-Dixon furnace, now under consideration, and all facilities for rolling its billets into desired shapes. Later the present 5-ton furnace will be removed to the new plant. A complete modern plant, capable of expansion, will be the result. It is the belief of the promoters of this furnace that the large electric furnace unit as a successful competitor with the open-hearth is a development to be confidently expected.

SWELLS AND SPRINGERS.*

By DR. L. M. TOLMAN,†

As a result of the president's address at the last meeting and recommendations made by him, a committee was appointed to report to the association on a resolution comprehending three questions: (1) the cause of swells and springers; (2) the extent of their use; (3) should any of them be used for food?

In order to answer any of these questions we must know what kind of food products are included under the term of "swells and springers." Practically all classes of spoiled can goods are included, spoiled from numerous causes—as leaky cans, incomplete sterilization, use of bad material, poor tin, action of the food on the tin, bad methods of manufacture, damage from fire or water and many other causes.

The committee has in a rough way classified "swells and springers" under six different heads:

1. The plainly developed swells due to decomposition of the food.

2. Incipient swells where a slight decomposition has taken place, and the bulging of the cans is not marked.

3. What are known as "flat sours," which are decomposed due to an acid fermentation without the production of noticeable amounts of gas.

4. The product which might be called a gas swell springer, due to the development of gas resulting from the action of the acidity of the product itself upon the metal of the container.

5. A type of swelled can which may be called a springer but which is due entirely to overfilling the can when originally packed or to incomplete exhaust at that time.

6. Can-damaged goods. By this is meant cans the contents of which are sound but the outside has become rusty or the labels have become dirty or unsightly in appearance.

Can any of these various classes be used for food? It seems to be the universal opinion of food officials and of the consumer that swelled can goods are not fit for food purposes. Whether or not all such products are injurious to health may be subject to doubt, but in our opinion they should all be excluded because of their inherent danger and the impossibility of making a determination of whether bacterial action has produced a harmful or harmless decomposition.

Swells due to overfilling or improper exhaust, and to these causes alone, are edible and suitable for food.

It seemed to the committee that the first thing to provide would be a scheme for differentiating the good from the bad so that a separation could be made. This matter was taken up with Dr. Bigelow of the National Canners' Laboratory and a scheme prepared which

*Paper presented at recent Food Commissioners' Convention, Detroit, Mich.

†Chief of the Chicago Laboratory of the Bureau of Chemistry.

would guide the inspection in separating swells due to decomposition, from swells due to acid reaction or swells due to overfilling or insufficient exhaust.

The third question asked of the committee was as to the extent of the use of these spoiled goods as food or in the manufacture of food products. This question presents two fairly clear-cut lines.

First. Local sale at point of origin, chiefly in the larger cities.

Second. Reprocessing or sale of returned rejecteds.

We were able to obtain during the year evidence in about 25 cases where spoiled can goods in large quantities were either reprocessed or sold for use in manufacturing food products, and these cases occurred in 10 to 15 different states and represented widely different products.

These instances, together with the reports of experience of food commissioners, show that this traffic is sufficiently large that something very definite should be done to regulate it.

As to the local traffic at points of origin it was found there was about three ways by which the peddlers, cheap restaurants and other users obtained their supply; first, directly from the grocer; second, indirectly from the grocer through the agency of men employed to carry them to the dump, and, third, through the collection from the dump of goods which had not been properly destroyed. The facts obtained very strongly impressed the committee that much greater care should be employed by food officials, grocery men and the trade in general in seeing that condemned goods are actually destroyed, or denatured.

As to the use of these goods we find that they are either peddled around to the poor grocery stores, cheap restaurants or boarding houses. The returned spoiled goods, which again go into trade, are to a large extent used in the manufacture of other food products.

Local distribution must be met by the city and state inspection service. As to the return of spoiled canned goods to the jobber or manufacturer, the committee felt that it should know more about the extent of this traffic and through the assistance of the National Wholesale Grocers' Association was able to obtain what we believe is a reliable estimate.

Five hundred replies were received from wholesale grocers all over the country to the following questions:

1. Approximately what percentage of swells and springers were found in your canned goods during the calendar year of 1915?

2. What percentage of said swells and springers were returned to the packers?

These replies show that less than 2 per cent of the entire output resulted in returns for damaged goods; 55 per cent of the 500 returned their rejected claim goods; of this 55 per cent some returned all of their damaged goods and others only a portion. As nearly

as we could estimate from the replies; approximately 51 per cent of the firms returned 50 per cent or a less amount. From these estimates it would appear that only about 25 per cent of the rejected canned goods were actually returned to the canner; or, in other words, 75 per cent of the goods upon which claims were made was released to the retail or the wholesale grocer, as the case may be, after the claims were adjusted. It is this released stock which becomes a source of supply for the local trade such as peddlers and cheap grocery stores.

In order that the Association may have all of the facts before it in considering this question, the committee has prepared the following summary of the reasons why the packers require any of these spoiled goods to be returned.

1. The manufacturer desires to identify the goods and allow only such claims as are correct and also to prevent more than one claim for the same lot of goods.

2. He desires to ascertain the age of the stock and prevent claims for goods which are held over the guarantee period.

3. He desires to see that retailers do not receive credit for goods and then be in the position to release them and sell them to peddlers or reproducers or salvage dealers.

4. He desires the return of certain classes of the goods so that he can make an investigation to determine the cause of the spoilage—whether it is due to understerilization, defective sealing, improper cans, the packing of impure material, or whatever the cause may be.

5. To look over the various returned goods and take out that portion which is sound and suitable for food.

These arguments are undoubtedly reasonable and legitimate but the committee cannot escape the fact that in their opinion all such shipments of decomposed canned foods in interstate commerce are in violation of the Federal Foods and Drugs Act. How then can these legitimate demands of the trade be met as they should be met?

The committee recommends that the subject be considered another year in connection with a joint committee from the various branches of the trade with the object of submitting a detailed recommendation at the next meeting of this association. It has been suggested that all claims for damaged goods might be sent to the State Food Commissioner so that he may control the disposal of the goods in question; that certain points in the states might be designated for the collection of these goods, where claims could be adjusted, the goods salvaged, and the goods which are spoiled, destroyed under supervision.

Such a supervision would obviate (at least in part) the need for the return of spoiled goods, now sought by the manufacturers.

There is a very strong sentiment in the food control of states and cities opposed to any plan which will

permit the return or shipping of these spoiled goods in commerce, and which will not require immediate destruction or taking out of the channels of trade any decomposed can goods. The evidence collected by this committee amply supports these objections. It would seem that the only solution of the problem would be something along the line of a proper control and destruction of the goods under supervision at point of detection.

The committee has reached the following general conclusions as the result of their investigation during the past year:

1. Swelled can goods due to decomposition should not be used for human food nor in the manufacture of food.

2. Swells which are due to acid reaction of the food upon the container should not be used for food until further investigation, and certainly it should be determined whether or not any of the gas pressure found in the product is due to decomposition.

3. A very determined effort should always be made by food control officials to separate this stock into the good and bad portions, and to distinguish between swells due to decomposition and those which may be due to overfilling or improper exhausts. However, attention should be brought to the fact that the question of overfilling is becoming very much less important, as the manufacturers are rapidly finding out just how much to put into the cans, so that possibly this will not be a serious matter.

4. There is an extended traffic in swells and spoiled can goods, especially in the large cities, the source of supply of which is the rejected can goods from grocery shelves, fire or water damaged stock.

It is believed that this traffic is a decided menace to the public health and that some means should be definitely and clearly devised so that there will be uniform action against products of this kind by the city, state and federal governments.

5. There is need of much greater care by food control officials, city, state and national, and by reputable wholesale grocers and retail grocers, to see that condemned canned goods are actually and completely destroyed or denatured, as a very large source of the supply at the present time is through the illegitimate recovery of goods which have been condemned and which it was the intention to destroy.

6. Some means should be provided by which certain classes of spoiled canned goods can be returned to the manufacturer when the question as to the cause of the spoilage is to be investigated.

7. The reprocessing of swelled canned goods where the swelling is due to decomposition is not a legitimate practice and should not be permitted.

The committee presents this as a preliminary report, with the recommendation that the committee be continued to make a further report at the next meeting, at that time to submit as detailed a plan as possible

by the best method of handling this problem, and that the committee be authorized to co-operate with the committees from the trade in working out this plan.

THE 53RD MEETING OF THE AMERICAN CHEMICAL SOCIETY.

Further details regarding the meetings of the American Chemical Society and associated bodies to be held in New York City, Sept. 25 to 30, are now available.

The meeting will be held in conjunction with the Second National Exposition of Chemical Industries. The American Electrochemical Society and the Technical Association of the Pulp and Paper Industry will hold meetings in New York City during the same week. It is expected that 2,000 to 2,500 chemists will be in attendance during the week's exercises, and that this meeting of the American Chemical Society will be the banner chemical meeting of the world.

The following is a list of the chairmen of local committees. The names of all the members of the committees will be printed in the final program: Executive—J. Merritt Matthews, 50 East 41st street, New York City. Finance—L. H. Baekeland, Snug Rock, North Broadway, Yonkers, N. Y. Registration—H. R. Moody, College of the City of New York. Reception—To be announced. Entertainment—E. G. Love, 124 East 15th street, New York City. Hotels—T. J. Parker, 92 William street, New York City. Press and Publicity—Allen Rogers, Pratt Institute, Brooklyn, N. Y. Ladies' Committee—Mrs. L. H. Baekeland, Snug Rock, North Broadway, Yonkers, N. Y.

The registration office will be open at The Chemists' Club, 52 East 41st street, throughout the week. The society headquarters will be at The Chemists' Club, 52 East 41st street; hotel headquarters, Hotel Astor, 43rd street and Broadway.

The final and complete program will be sent on or about Sept. 18. The Second National Exposition of Chemical Industries will open at 2 p. m., Sept. 25. The official opening of the American Chemical Society meeting will take place at 10 a. m., Sept. 26 at the Horace Mann Auditorium, Columbia University, Broadway and 117th street.

The Second National Exposition of Chemical Industries is already an assured success, two whole floors of the large Grand Central Palace having already been engaged, with prospect for the third floor. Practically all the large chemical industries of America will have exhibits which will offer an unexcelled opportunity for study to American chemists. There will be no entrance fee charged to members of the American Chemical Society. The member's badge obtained at the registration desk will admit him at all times.

The American Chemical Society, The Chemists' Club, American Institute of Mining Engineers, Amer-

ican Electrochemical Society, and the Technical Association of the Pulp and Paper Industry will all have booths at the Exposition. The Bureau of Commercial Economics is collaborating in arrangements for a motion picture program at the Exposition. The Exposition will also have two large sections given over to the "Southern Opportunity" that awaits the industrial chemist, and a large section of exhibits for "The Paper and Pulp Industry." The program includes the following:

Monday, September 25.

- 2:00 p. m.—Official opening of Exposition, addresses by Dr. Chas. H. Herty, Dr. Francis A. J. Fitzgerald and Dr. Arthur B. Daniels.
4:00 p. m.—Council meeting, Chemists' Club.
7:30 p. m.—Council dinner, Chemists' Club.
9:00 p. m.—Council meeting, Chemists' Club.

Tuesday, September 26.

- 10:00 a. m.—General meeting of the Society at Horace Mann Auditorium, Columbia University, 117th street and Broadway. Addresses of welcome by Mayor Mitchel of the City of New York, President Butler of Columbia University. Response by President Herty, followed by general papers.
2:00 p. m.—Public meeting, Horace Mann Auditorium, Columbia University. Addresses by speakers of national reputation (to be announced). Presidential address by Dr. Herty.
8:00 p. m.—Reception at Hotel Astor. Members American Electrochemical Society invited.

Wednesday, September 27.

- Morning—Divisional meetings, Columbia University. Symposium on Colloids (theoretical).
Afternoon—Industrial Conference, Chemists' Club. American Dye Stuff Manufacture. Industrial Conference, Grand Central Palace. Steel Alloy Metals: Electric Steel.

Thursday, September 28.

- Morning—Divisional Meetings, Columbia University. Symposium on Colloids (applied).
Afternoon—Industrial Conference, Chemists' Club. Industrial Alcohol, Acetone and Formic Acid. Industrial Conference, Grand Central Palace, Glassware and Porcelain.
Evening—Invitation Smoker of the American Electrochemical Society.

Friday, September 29.

- Morning—Divisional Meetings, Columbia University. Symposium on Occupational Diseases in Chemical Trades.
Afternoon—Industrial Conference, Chemists' Club, Medicinal Chemicals. Industrial Conference, Grand Central Palace, Manufacture of Paper Pulp and By-Products.
8:00 p. m.—Subscription Banquet at Waldorf-Astoria.

Members and wives, \$3.50; guests at cost (probably \$7). Members American Electrochemical Society and Technical Association, American Pulp and Paper Industry invited, with cost same as to members American Chemical Society.

Saturday, September 30.

- Morning—Meetings of Divisions. Industrial Conferences. Chemists' Club, Oils and Motor Fuels. Industrial Conferences, Grand Central Palace, Miscellaneous Chemical Industries; Convertibility of Plant.
11:00 p. m.—Exposition closes at Grand Central Palace.

DUST EXPLOSIONS IN GRAIN SEPARATORS.

A large number of fires and explosions in grain separators during the threshing process has occurred in the Pacific Northwest during the last two seasons. The U. S. Department of Agriculture has for some time been conducting studies relative to the cause and prevention of dust explosions in grain mills, elevators and similar plants. The close relation of these thresher explosions to the general study of grain dust explosions led to the inauguration of a special study of this allied problem in the Northwestern field during the 1915 season. The investigations were conducted by the Bureau of Chemistry and the Office of Public Roads and Rural Engineering and the results are given in a recently issued bulletin.

In all 166 occurrences were investigated and reported. The results of the investigation indicate that the wheat crop contained a large percentage of smut and that the explosions and fires in many cases were due to the formation of an explosive mixture of smut dust and air and the ignition of this mixture by static electricity during the threshing operations.

In each explosion and fire the investigator summarized the evidence obtainable, and after careful consideration of all information available assigned the cause most probable in his opinion. The following summary shows the conclusions reached in 94 special cases investigated:

Static electricity	45
Smut explosion	25
Friction sparks	10
Matches	5
Doubtful	5
Teeth striking	1
Incendiary	1
Beater striking conveyor	1
No clue	1

94

About 75 per cent of the occurrences were assigned to the presence of static electricity and to smut explosions. The percentage assigned by the investigators as indicating incendiary origin was very small as compared with that advanced by local men.

The percentage of smut present in the wheat crop was determined in each case by taking a sample of a known number of heads and separating it into two

parts, one consisting of those heads which were not affected by smut, the other part of those heads which were affected. The proportion of smutted heads to the whole number of heads in the sample gave the percentage of smutted heads present in the crop.

Of 112 explosions nearly all occurred during the threshing of grain which contained from 1 to 35 per cent of smutted heads; the average percentage in 108 explosions was 15. There were only three explosions in fields reported to contain no smut.

Percentage of smutted heads.	No. of explosions.
No smut	3
Less than 1 per cent.	4
1 to 5 per cent.	19
5 to 10 per cent.	27
10 to 15 per cent.	15
15 to 20 per cent.	20
20 to 25 per cent.	8
25 to 30 per cent.	7
30 to 35 per cent.	5
Not known	4

It was evident from the beginning of the investigation that a large quantity of static electricity was generated during the operation of the separator. Workmen admitted that on certain days static electricity was noticeably present around the machines.

One case in which the owner thought the presence of static electricity was responsible occurred in Latah County, Idaho. This machine was new, having been operated but part of a day. It was completely destroyed as a result of the explosion. As the outfit was located 15 miles from a railroad and 4 miles from the county road there was no reason to suspect incendiarism. The crew was composed of neighbors, or men known to be reliable. There was 19 per cent smut (estimated by counting the smutted heads) in the crop. The weather was very hot and dry. After summarizing the evidence, the investigator concluded that it was clearly a case of smut explosion by electrostatic ignition.

A similar case occurred in Whitman County, Washington. The owner had experienced two fires, one in the evening and the other the following morning, neither of them causing much damage to the separator but destroying the surrounding grain in the field and the threshed grain in stacks. At the time of the occurrence the machine was threshing wheat with 31 per cent smut and was located 21 miles from the railroad and several miles from the county road. The evidence available convinced the investigator that the explosion was due to ignition of smut dust by static electricity.

In another case the owner of a machine which was destroyed stated that he was standing at the engine and was looking directly at the cylinder at the time of the explosion. He could see the cylinder itself, as the feeding had stopped momentarily. He observed a long blue spark coincident with the explosion. In other investigations the men in charge of the machines stated that there were large quantities of static electricity present around the machine preceding the explosions.

In one case the owner of the machine stated that

his machine was very heavily charged with static electricity on the morning of the explosion, to such an extent that it was not possible to touch any metal part without getting a shock. This condition had never been noticed on this particular machine before. The explosion was violent in nature and totally destroyed the machine.

Previous investigations relative to the causes of explosions in grain mills and elevators and similar plants indicated that static electricity was a possible factor in the production of dust explosions.

In September, 1913, at the time investigations were being conducted in co-operation with the Millers' Committee of Buffalo, N. Y., two slight explosions occurred on a dry, frosty morning in early fall, in two separate plants in western New York, at a time when the feed had been shut off from certain grinding machines. Both occurrences took place a considerable time after the stream of grain had stopped entering the machines. The possibility of static electricity being generated by the operation of the revolving plates of the machine suggested itself in a very preliminary way at the time of these explosions, and a confidential report was prepared and presented at the time to the Millers' Committee. Although up to that time no record could be found that experiments had been conducted to determine whether cereal dusts could be ignited in this manner, it was found by experiment that sufficient static electricity could be generated by the friction of a very small pulley and belt to ignite natural gas readily. It was learned at this time that a milling company in the South, engaged in grinding cottonseed cake into meal, after experiencing a series of explosions, had prevented a repetition of these occurrences by grounding the machine by means of a wire connected to a rod driven into the ground near by.¹ This seemed to confirm the original theory and indicated the value of a grounding device of this kind.

The possibility of static electricity as a source of cereal dust ignition was very clearly established by an explosion in the dextrine department of a starch factory in one of the eastern states (in September, 1914). The origin of this explosion was traced to the generation of static electricity by friction of particles of dextrine on an 80-mesh brass gauze surrounding a revolving reel. This reel was revolving at the rate of only 16 revolutions per minute when the explosion occurred.

At the time of the explosion this reel was grounded to an overhead sprinkling system. During the investigation which followed, however, it was found that the connection was made from the journal box, and that a heavy film of fresh oil surrounded the shaft. This was thought to have served to insulate the shaft and allow the static electricity to accumulate within the reel until there was sufficient charge to ignite the dust.

¹Preliminary Report on the Explosibility of Grain Dusts. Co-operative Investigation by Millers' Committee, Buffalo, N. Y., under the direction of Dr. George A. Hulett, Chief Chemist, U. S. Bureau of Mines. By David J. Price and Harold H. Brown. Pittsburgh, 1914.

An English scientist has determined that if a cloud of dust is blown against an insulated conductor (a wire, for instance) the wire becomes charged with electricity, and under certain conditions may become so highly charged as to give off sparks.²

RESEARCH, SCIENTIFIC AND INDUSTRIAL IN THE COAL-TAR DYE INDUSTRY.*

By BERNHARD C. HESSE.

The coal-tar dye industry as it stands today is the result of the methodical and systematic following up of a side-issue of a scientific research in 1856. It is the composite result of the co-ordination of science, industry and merchandizing. The purpose of this paper is to consider the contribution of chemical research to this net result and to compare, in some manner, the contributions of investigations in institutions of learning with those of investigations in industrial establishments.

Chemical research is, without doubt, the real underlying source of the origin, development and growth of this industry: on account of the great brilliancy of the intellectual achievement in synthetically producing on a commercial scale a thing theretofore derived wholly from vegetable sources, namely, alizarin, and of producing so many beautiful and useful things from such an unsightly mess as coal tar, the part played by research in this development has come to be regarded by the public as distinctive of and peculiar to this industry and naturally this has lost nothing in the retelling; so it is not to be wondered at that research in coal-tar dyes came to be spoken of by both laymen and scientists as something of an extraordinary nature. This view has become very widespread and deep-rooted. From the time I first became acquainted with coal-tar dye chemistry at the University of Michigan in 1888, until I was graduated from the University of Chicago in 1896, I somehow acquired from the literature and from my instructors the idea, amounting almost to conviction, that there was something almost uncanny about coal-tar dye research and the methods employed in it.

Directly after graduating from the University of Chicago in 1896, I entered the employ of the largest coal-tar dye works in the world at its plant in Germany and indeed in one of its research laboratories. This was my first trip outside the United States and it was, of course, an event of the first magnitude for me to be in Europe, and, as a chemist, to be in Germany, in a German coal-tar dye plant, and to cap it all in its research laboratory—a real *sanctum sanctorum* for chemists. In a short time the daily routine

wore the novelty off my experience and I then settled down to calm analysis and dispassionate appraisal of my surroundings and to compare what was actually before and around me with my expectations. I found that the general laboratory equipment was no better than what I had been accustomed to; that my colleagues had no better fundamental training than I had enjoyed nor any better fact—or manipulative—equipment than I; that those in charge of the work had no better general intellectual equipment nor any more native ability than had my instructors; in short, there was nothing new about it at all, nothing that we did not have back home, nothing—except the specific problems that were engaging their attention, and the special opportunities of attacking them. Those problems were of no higher order of complexity than those I had been accustomed to for years, in fact, most of them were not very complex from a purely intellectual viewpoint. There was nothing inherently uncanny, magical or wizardly about their occupation whatever. It was nothing but plain hard work and keeping everlastingly at it. Now, what was the actual thing behind that chemical laboratory that we did not have at home? It was money, willing to back such activity, convinced that in the final outcome, a profit would be made; money, willing to take university graduates expecting from them no special knowledge other than a good and thorough grounding in scientific research and provide them with opportunity to become specialists suited to the factory's needs. However, we then had numerous men at home, who put their money behind investigational enterprises but they had selected subjects different from coal-tar dyes; for example, sewing machines, agricultural implements, typewriters, shoemaking machinery, incandescent lamps and many others, where the sums invested, the high-grade specialists employed, the scientific, systematic and methodical development and merchandizing lose nothing whatever by comparison with what is done in coal-tar dyes in Germany. This was my first conclusion 20 years ago and it has since been confirmed by comparison with conditions on both sides of the Atlantic and has long since become a firm conviction with me, fortified as it is by close and intimate contact with a number of large enterprises at home and ten different trips to Germany, covering a total of 36 months' residence in Germany, where and when I checked up my views. Also, I have met competitively and collaboratively coal-tar dye chemists and researchers, not only of Germany, but of Austria, France, Switzerland and England as well, and have worked side by side with them in three different research laboratories, two in Germany and one in England. Each trip brought me home more convinced than ever that neither Germany nor any of these other countries had anything fundamental to teach us in the way of research even though, as a people, we did have much to learn, particularly from Germany, in determination to know how to make everything count to its utmost profitably realizable

²Philosophical Magazine, London, 6 (1913), p. 481-494. "On the Electrification Associated with Dust Clouds," by W. A. Douglass Rudge, Professor of Physics, University College, Bloemfontein.

*Address delivered on June 5 at the Chemistry Conference at the 25th anniversary of the University of Chicago.

capacity, and to make specialists out of university graduates—in other words, national teamwork.

In short, we have as good educational institutions, as good chemical instructors, as good chemical investigators, and as good native ability as has Germany or any other country, but with us these are not as widely diffused.

In the final analysis "Research" is made up of "I want to know" and "I am going to find out,"—two qualities which the American people, inclusive of its chemists, have always had in abundance and to spare, but not always co-ordinated nor efficient. Desire to know cannot have practical effect unless opportunity to find out be available. Today's opportunity was generally yesterday's impossibility. If opportunity ever presents itself in this country to find out about coal-tar dyes. I am confident that we will find out all that such opportunity can be made to make available and without going beyond our own borders for the men or the "know-how." What we do not have now, our own educational institutions are fully capable of supplying, if and when called upon. But in this, as in all like things, the time element is one that must be taken into serious account.

Like coal-tar dyes, our sewing machines, incandescent lamps, agricultural, writing and shoemaking machines are not natural products and had to make their own way in the markets of the world; they too had to be created and developed; as in coal-tar dyes every other country had the same initial opportunity to make the same kind of machines that we did, but we created those industries and we have maintained our supremacy against the world. It is nothing unheard-of or new for us to create new things, overcome long-standing prejudices and to conquer foreign markets.

Fundamentally then, we have done all the things that made the coal-tar dye industry, but our efforts have been along other specific lines; it merely remains for us to decide definitely to attack that particular problem, it is no harder to solve than many others that we have solved. It is not, and probably never has been, a question of whether we can or cannot make coal-tar dyes or whether we could learn how, but rather a question of when we did do it would it be worth our while; could we not do something else to better advantage?

In the coal-tar dyes industry as it is today, all but two of those dyes are without counterpart in nature; they are as much man-created as is a sewing machine or a typewriter. Two of the dyes now made from coal tar were, prior thereto, secured entirely from vegetable sources and had been used for centuries as dyestuffs: these two are alizarin and indigo. The coal-tar product is identical with the vegetable product in both cases. It was chemical research that pointed the way for the founding and development of this industry in both the above branches.

As applied to chemistry, research may be scientific, empirical or industrial; it is as impossible to draw the dividing line between these three classes as it is to designate the precise instant of time when night ceases and day begins, or the reverse. The scientific research of today is the empirical research of tomorrow and the industrial research of the day after.

Indigo and Alizarin.—In the case of both indigo and alizarin, scientific research first of all had to determine the chemical constitution of these substances and confirm them by a synthesis; then empirically, and guided by the spirit and method of scientific research, the commercially possible syntheses had to be explored and then industrial research had to adapt one or more of these methods to commercial use—a general procedure fundamentally familiar to Americans in many other lines.

Scientific research attempted to solve the chemical constitution of alizarin as early as 1848; in 1852 a constitution, since recognized as erroneous, was assigned to it but in 1860 its correct constitution was deduced and its synthesis from anthracene accomplished; its commercial introduction was accomplished within one year; empirical research, in less than six months from the discovery of the first synthesis, developed the method which, with but few nonfundamental changes, is the one used today, and shortly after its discovery the annual value of its production was \$8,000,000; that is, 20 years were required to solve the scientific research, and less than 1 year was needed for commercial introduction. Vegetable alizarin was practically conquered in less than two years of commercial effort, or a total of 22 years.

Scientific research into the chemical constitution of indigo began in 1841 and was not concluded until 1882; in 1890 empirical research led to the present-day commercial process, but it was not until 1897 that the industrial research was concluded; it required five years in addition to conquer vegetable indigo; that is, the scientific research required 41 years to complete its task, empirical research eight years, industrial research seven years, and commercial exploitation five years, or a total of 61 years. The annual value of vegetable indigo in 1882 was about \$20,000,000.

The contribution of scientific research was not limited to the ascertainment of the constitution of these two substances. In the case of alizarin the use of caustic-alkali melt of sulfoacids for the making of hydroxyl derivatives was discovered in the course of scientific researches in France and in Belgium in 1867, and applied in Germany and in England almost simultaneously in 1869 for making alizarin.

For indigo, liquid chlorine—in 1890 an industrial fact—was the direct offspring of a scientific research (though carried out in an industrial establishment) into the conditions under which chlorine can be liquefied and into the properties of liquid chlorine itself; the conversion of phthalimid into anthranilic acid was accomplished in 1890 in Holland by applying to

phthalimid a reaction originally applied in Germany in 1882 to acetamid and thereafter largely developed by chemists in Holland and elsewhere; the use of phenylglycine and of its carboxylic acid as an indigo intermediate was discovered in Switzerland in 1890; the use of mercury in connection with sulphuric acid for oxidizing organic substances controllably, as well as to complete oxidation, was discovered in 1883 and is of Danish origin, but was not applied to the oxidation of naphthalene until 1896. Therefore, scientific research also blazed the way for the commercial alizarin synthesis and provided the direct fundamentals of four of the necessary things in the first commercially successful indigo synthesis.

Furthermore, before the makers of synthetic alizarin and of synthetic indigo could afford to commit themselves definitely and heavily to the production of these two things, it was necessary to make reasonably sure that the particular method to be operated was as cheap as any as would be likely to be developed by others and above all that there were no "next-door-neighbors" chemically known as isomers, homologues and substitution products, that would be better than these two substances or either of them. Here is where the results of scientific research through its achievements in determining the possible number of isomers, homologues and substitution products enabled the empirical investigators to delimit and circumscribe the field to be investigated with reasonable assurance as to accuracy and certainty that nothing had been overlooked, that nothing was left for those who came after to create unwelcome effective competition—and in these empirical investigations the laboratory, investigational and reasoning methods of scientific research were liberally drawn upon.

Magenta and Its Congeners.—Passing now to those coal-tar dyes not to be found in nature, *i. e.*, the created dyes of this industry, it may be said that for the great majority of them the chemical constitution is assumed as known, based upon the methods of their production and the rules in relation thereto which scientific research established; to some of these dyes no chemical constitution has been assigned and for some even the chemical composition is not known.

Magenta was first discovered in Russia in 1856; chemists in France and England from 1858 to 1860 developed and patented various methods of manufacture from the commercial anilin of that day; but it was not until 1864 and 1866 that it was discovered that pure anilin or pure para or orthotoluidin when treated by these methods would not yield magenta but that a mixture of these three is needful; it was not until 1878 that its constitutional formula was determined. Long prior to this the industrial method of today had been found by empirical or exploratory research; the constitutional formula, however, gave greater certainty to the conclusion of the industrial men that the limit of successful further investigation had been reached for at least a reasonably long period of time. In this

case, knowledge of the constitution did not itself point to any commercially new or useful results; it merely confirmed the conclusions as to temporary finality of the work of others.

Long before the constitution had been determined it was definitely ascertained empirically by men in France and England, and to a lesser extent in Germany, that there were three amido groups in magenta, and long before that, that there were replaceable hydrogens in magenta and the empirical workers had exhausted the then available means of treatment of magenta for its substitution products and had worked out substantially all the commercially useful products which included red, blue, violet and green, both basic and acid, of the present day.

As a direct result of the scientific investigation for the constitution of magenta came the investigation of condensation products of benzaldehyde with tertiary amines and from that the use of benzaldehyde and of substituted benzaldehydes in the making of dyes which have since acquired great commercial importance. Once the direction was given, it was only necessary to prepare the various substituted benzaldehydes and the substitutes for dimethylanilin employed in making the pioneer of this class in 1878 and systematically to exploit the field thus marked out. In 1878 it was recognized that nitration and reduction might yield new dyes but attempts in this direction then failed only to become commercially successful about ten years later.

In a scientific investigation into the constitution of rosolic acid in 1878 it was found that dioxybenzophenone combines with phenol to produce aurin. Michler's Ketone, a "next-door-neighbor" of dioxybenzophenone, was discovered in 1876; its production on a commercial scale was realized in Switzerland in 1883, in which year it, like benzaldehyde in 1878, was treated, also in Switzerland, with dimethylanilin and gave a violet. From then on it was only needed to treat Michler's Ketone with all the substitutes for dimethylanilin and to work out the commercially useful dyes in the field thus laid out—a labor not completed in the 33 years that have since elapsed.

The Phthalicins.—All of these investigations reflect the influence of the scientific researches begun in 1871 on the behavior of phthalic acid with phenols in which the trihydric phenol, pyrogallol, was first examined, then the dihydric phenol, resorcin, and, finally, phenol itself; the commercial introduction of the first did not take place until seven years later, while the second required three years, this delay being due to the difficulties encountered in commercially making the intermediates, namely, phthalic anhydride and the phenols; the bromination products of fluorescein, though discovered in 1873, were not marketed until 1874; these were thereupon followed by iodination, methylation, chlorination and nitration products of fluorescein, but it was not until 13 years later, or in 1887, that alkylated amidophenols were investigated

in their behavior towards phthalic acid and yielded most valuable dyes; still, not until 1894 or seven years later was it discovered that this reaction proceeded in a two-stage manner, combining first in equimolecular proportions and this result then reacting with the second molecule of the amidophenol, although such behavior was foreshadowed in the work done in the scientific investigation of the constitution of magenta and the synthesis of the benzaldehyde dyes and the dyes from Michler's Ketone just considered. While in this particular case, failure to recognize the two-stage character of the reaction did not result in the loss to the art of really valuable dyes, yet our knowledge of the mechanism of this reaction was by that much retarded. In the case of tartrazine, which was discovered in 1884 and marketed in 1885, although its two intermediates were known to scientific investigators wholly as the direct result of abstract scientific work as far back as 1879, the two-stage nature of its synthesis was not observed until 1893, or nine years later; in this case the two-stage process enables the production of commercial dyes of real value not theretofore available.

Methylene blue, discovered in 1876 and marketed in 1877, was manufactured in three different ways before conclusive answer was obtained as to the mechanism of any of these reactions by scientific examination, in 1889; no method of manufacture, at all new in principle, grew out of this investigation.

The Azo Dyes.—The reactions underlying the azo dyes were exhaustively treated, scientifically, in researches begun in 1860 and completed in 1870; the reactivity of diazo compounds with amido compounds was discovered in 1864 and with phenolic compounds in 1870. The first of the azo dyes appeared on the market in 1861 and was followed in 1863 and 1875 by two others, but it was not until 1876 that this reaction began to be exploited to any considerable extent and here again the reason was the difficulty of obtaining the intermediates in commercial quantities. All products of this class were direct dyes for wool or mordant dyes for cotton and none of them was a direct dye for cotton until 1884, when benzidine, itself described in scientific literature as early as 1846, was found to be capable of producing direct cotton dyes; but these first benzidine dyes were not very fast to acids, alkalis or light and the chase for phenolic or amido or amidophenolic substances which, when combined with benzidine or benzidine substitutes, would yield fast colors, was on! In this chase scientific investigators contributed little of effective specific help; they had marked out the field, provided the general implements, intellectual and manipulative, but the magnitude of the problem was too great for any individual and one wholly unsuited to university treatment; its solution called for careful preparation of the individual materials, combining them with benzidine and benzidine substitutes, to yield direct cotton dyes, examining these dyes in their behavior towards cotton

and other fabrics under service conditions or their substitutes and, profiting by whatever they showed, forecasting further work with the help of the general scientific rules and laws of structure of these materials and to take up the task anew. A heart-breaking, desolate and uninspiring lot for the isolated worker, not in the confidence of those who know commercial conditions as to the availability, immediate or remote, of the materials needed to make these new intermediates, and of the commercial requirements of the dye markets, but a task full of zest and excitement when carried out in co-operation and collaboration with those who were conversant with all these details—for it was clear that there could be but few victors, the laggards would be beaten. Surely, the university and the individual investigator were hopelessly outclassed in this particular chase for only the worst kind of a fluke could lead to a useful result; true, new results could be obtained, but differing to the uninitiated in such subordinate and seemingly trifling details as to make the work actually sheer monotony. Yet the greatest skill and knowledge was required of the men who actually carried out this work in the industrial establishments.

In the middle of the eighties investigation by individual investigators and by institutions of learning began to cease contributions of pioneer value to this industry and except for the brilliant glycine synthesis of indigo in 1890 the scientific researchers have done nothing since which specifically and directly approaches pioneer work. By that time research in this field had settled down to the humdrum task of sifting out from the hundreds of thousands of millions of possible dye combinations those that could survive in the world's markets. The work theretofore done by the university investigator was now done in industrial establishments and the new types of commercial dyes since then introduced have emanated from these industrial establishments themselves and as a direct result of industrial conditions themselves, and not from any real scientific experimentation, reflection or deduction by university investigators, as such.

However, looking backward, it does seem that industrial investigators could have developed the industry faster and that university investigators could have pointed out new fields a little more quickly than they did. For example, sulfonating as a means of rendering dyes better adapted for animal fiber, was discovered as early as 1862, yet Martius' Yellow, discovered and marketed in 1856, was not sulfonated until 1870, nor was magenta, also marketed in 1856, sulfonated until 1877; anilin yellow was not sulfonated until 1877, although on the markets in 1850; as early as 1876 it was known that sulphur could be substituted for the imido group to produce new dyestuffs, but this substitution in the indigo group was not tried until 1905, although all needful materials were known as early as 1890, and the real development of the indigoid dyes did not begin until well after 1900, although most

of the materials had been available for upwards of 10 years. Instances like these could be given in great numbers.

Of course, after things have been done it is not only very easy but most ingracious to say that they should have been done sooner or better, but these comparisons are not here made for any purpose of criticism or fault-finding; they are made in the hope that calling attention to a few opportunities now easily recognized as having been overlooked in the past, may sharpen our foresight and increase our powers of intellectual penetration and deduction and hearten university investigators so that they may again be the pioneer leaders in a field which is without limit and whose future cannot but be far brighter than its past, however glorious that has been. The opportunities for applying constructive imagination and selective judgment to the logical and systematic development of this field for pioneer work along the lines of types and subtypes are far greater today than they ever were and the chances of success are certainly no smaller than they were in the days when the university investigator was the guiding spirit in this industry. A comprehensive and useful answer to the question as to the casual relationship between tinctorial properties and chemical constitution has still to be given; no more powerful intellectual instrument than this could be devised and the university investigator has an almost equal chance, so far as materials, facts and facilities go, with his industrial brother, and so far as surroundings in sympathy with such work are concerned the industrial chemist or researcher is very greatly at a disadvantage; an insight of this kind should be as powerful in this branch of chemistry as the calculus is in engineering; the fact that more than 40 years have passed since the first attempts were made in this direction should not discourage—centuries before Newton and Leibnitz the world had many mathematicians of undoubted ability and power.

CONCLUSIONS.

It would be idle to suppose that in the foregoing anything more than a mere fragmentary outline sketch of the relative contributions of research and its various subdivisions to this industry have been given; nevertheless, the essentials are there, and they justify the following general statements:

I—The coal-tar dye industry had its origin in an accidental occurrence in the course of a purely scientific research.

II—For the first eight years the development was wholly through empirical research with no scientific or very clear guide to the field.

III—When scientific investigation had established certain fundamental scientific data the development proceeded more rapidly than theretofore and with greater certainty.

IV—The first individual success of real commercial magnitude and permanence owed its conception and execution wholly to scientific research.

V—Empirical investigation, both in institutions of learning and in industrial establishments, profiting by and taking advantage of purely scientific achievements and results, reached its conclusions and completed its labors more speedily and certainly than it otherwise would and made the commercial venture less hazardous than it otherwise would have been.

VI—The industrial research needed for the industrial application, itself, depended for much, and in some cases for all, of their material upon scientific research in no way connected with dyes or anything relating to them.

To return, then, to the beginning and fulfill the avowed purpose of this paper, namely, comparison of researches carried out in institutions of learning and in industrial establishments.

The university and like men for the first 30 or 35 years, by the development of the general and specific laws of chemical constitution, placed in their own and in the hands of industrial researchers means more powerful than ever existed as helps in chemical research; as a result, new methods of manufacture, new dyes and new types of dyes were made foreseeable long before the industrial researcher and chemist could get around to the experimental testing of the material thus laid bare.

The industrial chemist and researcher has not provided his university or scientific brother with any such broad general helps but he has contributed an enormous amount of fact material and has discovered a multitude of new manipulative methods but all of them more or less disconnected and not co-ordinated; the successful methods of industrial research were all borrowed from scientific research; for the past 25 or 30 years the industrial researcher has accomplished all new advances himself but in so doing he has drawn very heavily and without stint upon the results of scientific research not at all connected with the subject of dyes.

Who shall say which is the more important achievement? Both are wholly essential to progress; neither can develop to its fullest extent without the other; the scientific investigator needs access to an amount of fact-material which it is beyond his strength to gather; the industrial researcher needs rules, laws, generalizations, experimental and manipulative methods which his surroundings usually make impossible for him to discover or to devise; the coal-tar dye industry never would have existed without both.

This answer is probably the only one that should have been expected, yet the general and widespread opinion was and is otherwise. This answer portrays approximately the conditions existing in whole or in part in our own chemical, mechanical and electrical industries and in every application of science to everyday life, and why should chemistry applied to coal-tar dyes be different? The answer is that it is not.

Since our success as a nation in chemical, mechanical and electrical endeavor is in part, at any rate,

based upon essentially the same attitude towards their respective purely scientific branches and their commercial application, is not that a complete warrant for the conviction that we also have the ability to build up a coal-tar dye industry? Our institutions of learning have long been prepared competently to make their contribution should our industrials make the call. Will our industrials send forth the call?

NITRE CAKE AS A SUBSTITUTE FOR ALUM IN SIZING.*

In England there is talk among paper manufacturers of substituting acid sulphate of soda or nitre cake for alum in the sizing process. Sindall and Bacon refer to it in a recent number of the *Paper Makers' Monthly Journal*, saying the suggestion that crude nitre cake and commercial bisulphate of soda should be used as substitutes for alum points to the necessity of determining what quantity of such substitute is required for a stated amount, of example 1 ton or 1 cwt. of ordinary alum. The article continues as follows:

The crude nitre cake offered as a substitute is a mixture of acid sodium sulphate with normal sodium sulphate which contains a certain proportion of acid present in combination with the soda available for the precipitation of rosin from rosin size. The true acid sulphate represented by the formula NaHSO_4 contains theoretically 40.8 per cent of available acid, while the amount in nitre cake varies from 25 to 35 per cent.

If a solution of the true acid sulphate of soda or of nitre cake is added to a rosin milk the rosin is precipitated, leaving a clear solution, the reaction being somewhat similar to that produced by alum. The precipitate, however, is somewhat denser and of a different character to that produced by alum, and the sizing effect does not appear to be of the same order.

On a practical scale the proper addition of the nitre cake to the beating engine can be regulated by the ordinary tests for acidity, by means of litmus paper. The exact neutralization of the rosin size to the point at which the whole of the rosin is precipitated still leaves the solution alkaline so that by proper supervision of the process the danger of any excess of acid can be easily avoided.

The following figures will be of interest as showing the actual quantities required for precipitation:

Analysis of the Rosin Size Used—		Percent.
Moisture	50.7	
Free Rosin	12.0	
Combined Rosin	33.9	
Soda Na_2O	3.4	
	100.0	
Nitre Cake—		Percent.
Sulphuric Acid	24.5	

ANALYTICAL PROCESS.

A solution of the nitre cake of definite strength was made by dissolving 20 gm. in 200 cc. of water, so that

1 cc. of nitre cake solution equals 0.1 gm. of nitre cake.

The rosin milk was prepared by dissolving 10 grammes of size in 100 cc. of water giving a solution containing 0.1 gm. of rosin size per 1 cc. Titrated 10 cc. of rosin milk with the nitre cake solution until the neutral point was determined. This was effected by making a series of experiments using 10 cc. of size in each case, and adding varying quantities of nitre cake solution until the end reaction was complete. In each case the mixture was filtered and the end reaction found by determining the point at which the filtrate no longer showed any turbidity.

It was found that 10 cc. of size solution was precipitated by 1.85 cc. of nitre cake solution. In other words the relative quantities were as follows:

100 parts rosin size required for complete precipitation 18.5 parts nitre cake.

Under these conditions the solution was still alkaline and required the addition of further nitre cake before becoming acid. This is confirmed by the analysis of the nitre cake itself. It was found that 20 cc. of the nitre cake solution (equivalent to 2 gm. of nitre cake) required 10 cc. of normal alkali (equivalent to 0.31 gm. of soda, Na_2O). The amount of soda present in the rosin size as shown by the analysis is 3.4 per cent, so that from the soda figure it can be shown that 100 parts of rosin size requires 22 parts of nitre cake on the following basis:

0.31 parts of soda Na_2O = 2.0 parts of nitre cake. Hence 3.4 parts of soda Na_2O requires 22 parts of nitre cake.

We have already seen that 3.4 parts of soda Na_2O corresponds to 100 parts of rosin size.

The same procedure can be followed with regard to bisulphate of soda. In one case we found the bisulphate offered contained 33.8 per cent sulphuric acid (H_2SO_4). The rosin size used had the following composition:

	Percent.
Moisture	41.3
Total Rosin	52.5
Soda Na_2O	6.2
	100.0

On determining the equivalent quantities of these two materials the ratio was as follows:

100 parts of rosin size required 24 parts of bisulphate of soda for complete precipitation.

It is not possible to give a stated quantity of nitre cake for rosin size without a preliminary analysis of both materials, owing to the varied composition of the two. The foregoing figures, however, are some indication of approximate ratios which will be useful to the papermaker.

The Geological Survey, Department of the Interior, now has available for distribution its annual statement on Cement in 1915. The quantity of cement produced in the United States is given as 85,914,907 bbls., with a value of \$73,886,820.

*From Paper.

THE AMERICAN TEXTILE MANUFACTURER: HIS ATTITUDE TOWARD AMERICAN-MADE DYES.*

By FREDERIC DANNERTH.

So much has been said during the past two years regarding the attitude of American textile manufacturers toward American-made dyes that it seems necessary to correct some current impressions.

One of the principal, if not the most important, reason for using German-made dyes in the United States was the fact that nearly all the sunfast and laundry-proof dyes available were and are still made in Germany. The dyes used for printing colored stripes on men's cotton shirtings are the well known vat dyes which occur in commerce under the distinctive names of Helindone, Algole, Indanthrene, Cibacron. Then, too, there are a large number of "acid" dyes which are characterized by unusual fastness to light when applied to wool and silk fibers. These acid dyes if applied to silk fabrics can be exposed to direct sunlight for a period of 40 days, in a latitude of 41° North, during July and August, without showing any appreciable "fading." For the benefit of such research chemists as may be interested in developing dyes of this character, I have appended a list of some sunfast dyes together with the index number under which they appear in Schultz' "Farbentabellen" (1914 edition). This might well serve as a basis for advanced dye investigations in our organic chemical laboratories.

SUNFAST DYES ON ANIMAL FIBERS.

(865)	Alizarin cyanin green GX
(864)	Anthrachinon green GXN
(863)	Anthrachinon blue-green BXO
(862)	Alizarin blue-black B
(861)	Anthrachinon blue SR extra
(860)	Cyananthrol G
(859)	Cyananthrol R
(858)	Alizarin Saphirol B
(853)	Anthrachinon violet B
(852)	Alizarin Irisol D
(851)	Alizarin direct blue B
(850)	Indanthrene blue VB
(639)	Gallanyl violet RB
(303)	Brilliant yellow
(249)	Crocein scarlet 3B

These and a score of others including such well known dyes as Cloth Red and Naphthol Green are dyes which are today of importance to the textile manufacturers of the United States. To the list given might be added such dyes as Patent Blue (Hoechst) and Rhodamine (Elberfeld), which stand entirely in a class by themselves in the matter of brilliancy. The dyes mentioned have all been tested out in this laboratory and have been found to possess the properties mentioned.

In view of the extensive discussion of tariff protection for our American dye industry it seems that attention should be called to one of the important factors which has heretofore received no consideration in discussions of this measure. The industry of coal-

tar dyes is based on the science of organic chemistry, and this is a branch of chemical research which is at present being taught to only a limited extent at our American colleges. This statement is based on an inspection of the catalog of five leading universities located in the Atlantic States, and is supported by a personal contact with graduates of these institutions. It therefore seems timely to call attention to this deficiency in our educational system, and if possible provide ways and means for altering these conditions. The points which require emphasis are:

(1)—The supremacy of the German dye-manufacturing industry at the present day is probably due primarily to the advanced instruction in organic chemistry which is offered to students in German universities and technical colleges.

(2)—The manufacture of modern *sunfast* and *laundryproof* dyes in the United States cannot begin until there are in the country a sufficient number of men with an adequate education in the methods of organic chemical research.

(3)—Until this instruction is given in our American colleges, the extension of our dye factories and the invention of new and useful dyes must of necessity be very limited. Even if our college courses are revised today, it will be three or possibly four years before adequately trained men are available. The past twenty-five years of activity in our American dye factories bear abundant witness to the fact that our dye manufacturers are not inclined to spend time or money in the development of dyes of especial "fastness." This, however, is the particular point which European chemists have emphasized in all their dye developments and any rational consideration of tariff protection must take this point into consideration. The mere investment of capital will not insure for us an American dye industry.

(4)—The numberless complaints which have already been made with regard to the "fastness" of American-made dyes, demonstrate conclusively the present state of the industry in the United States, after an unhampered development of 46 years.

(5)—An investigation will show that European chemical laboratories, in the majority of cases, have their doors open from 7 o'clock in the morning until 6 o'clock in the evening. Which of our American universities can say as much?

The textile manufacturers of the United States have been variously accused by some of our less conservative collegiate professors, of favoring English and German dyes to the exclusion of American-made dyes. The answer to this accusation has already been given. All that the American dyer asks is that he be supplied with *modern dyes* which shall equal in brilliancy and in "fastness" the products which are now made by foreign manufacturers. It is also fair to assume that this will not be possible until students are given the necessary basic instruction in our colleges.

*Paper presented in April at the 100th meeting of the National Association of Cotton Manufacturers.

THE RELATION BETWEEN THE SPECIFIC GRAVITY OF ZINC CHLORIDE SOLUTIONS AND THEIR CONCENTRATIONS*

By E. BATEMAN.†

There have appeared from time to time tables giving the values for concentrations of zinc chloride. It is believed that a discussion of this subject would be of interest to the wood-preserver.

The specific gravity of a solution can be used to determine its strength with a fair degree of accuracy, provided the salt is pure, or of known purity, and further, provided that the temperature at which the specific gravity is taken is known. Under no other conditions are specific gravity measurements any more than rough approximations of the strength of a solution.

Nearly all salts, such as zinc chloride, sodium carbonate, etc., increase the specific gravity of a solution by approximately 0.01 for every per cent present in the solution. This is shown by the following table which gives the specific gravity of a number of 5 per cent salt solutions measured at 15° C., and referred to water at the same temperature.

Zinc chloride	1.046
Cobalt chloride	1.050
Copper sulphate	1.055
Ferric sulphate	1.043
Manganese sulphate	1.050
Manganese chloride	1.045

*From Wood-Preserving, the official organ of the American Wood Preservers' Association.

†Chemist in Forest Products, Forest Laboratory, Madison, Wis.

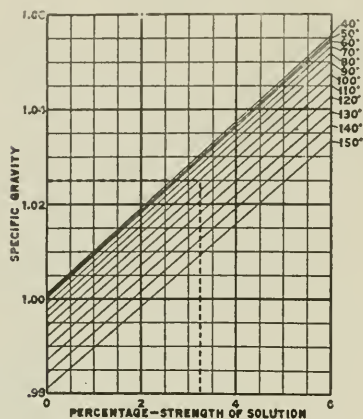
Sodium carbonate	1.052
Nickel chloride	1.049
Nickel nitrate	1.046

There are, of course, many exceptions to this, particularly the ammonium salts, acetates, etc., but it is a convenient figure and sufficiently accurate for our purpose. We can, therefore, say without serious error, that any salt solution having a specific gravity of 1.05 at 15° C. has approximately 5 per cent dissolved in it, but we do not know that this salt is pure zinc chloride, or sodium chloride, or manganese chloride, or ferric chloride. It may be any one of these, and many more, or it may be a combination of two or more and still have the same gravity, provided the total salt content is approximately 5 per cent, but if we know that a salt is 90 per cent pure and contains 10 per cent of other salts we can say that such a solution having a gravity of 1.05 contains roughly, 4.5 per cent of pure material, or 5 per cent of crude salt.

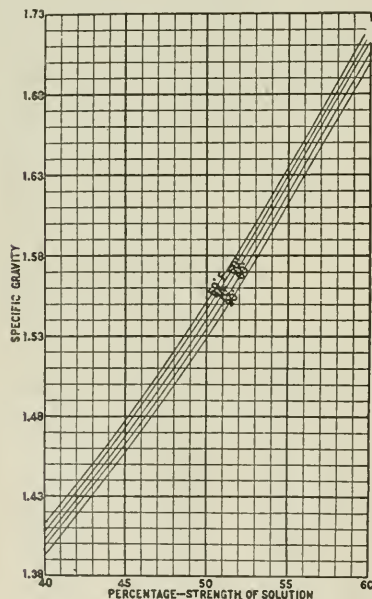
The importance of knowing the temperature at which the gravity is taken is illustrated by the following: If we take a water solution of salt having a specific gravity of 1.05 and raise the temperature to 100° C. it will then have a specific gravity of approximately the same as that of water at 15. In other words, our 5 per cent solution is now apparently only water by the hydrometer test, unless the temperature at which the hydrometer reading was taken is known. When the temperature is known we can correct for this expansion by the use of tables which have already been worked out, or in any case no very great error would be introduced if we used the tables for the expansion of water, provided we are working with dilute solutions, say 5 per cent or less. In some of our work

Sp. Gravity as Determined	STRENGTH OF ZINC CHLORIDE SOLUTIONS AT DIFFERENT GRAVITIES AND TEMPERATURES											
	Temperature—Degrees F.											
	40	50	60	70	80	90	100	110	120	130	140	150
	Strength of Solution.											
.990	...	...	...	...	...	...	...	...	.0	.3	.7	1.0
.992	...	...	...	...	...	...	...	.0	.3	.6	.9	1.5
.994	...	...	...	...	...	...	.0	.2	.5	.8	1.1	1.5
.996	...	...	...	...	...	.0	.2	.5	.7	1.0	1.4	1.7
.998	...	...	...	.0	.1	.2	.4	.7	1.0	1.3	1.6	2.0
1.000	...	...	.0	.1	.3	.5	.7	.9	1.2	1.5	1.8	2.2
1.002	.1	.15	.2	.3	.5	.7	.9	1.1	1.4	1.7	2.0	2.4
1.004	.3	.4	.5	.6	.7	.9	1.1	1.3	1.6	1.9	2.3	2.6
1.006	.5	.6	.7	.8	.9	1.1	1.3	1.6	1.9	2.2	2.5	2.9
1.008	.7	.8	.9	1.0	1.2	1.3	1.6	1.8	2.1	2.4	2.7	3.1
1.010	1.0	1.0	1.1	1.2	1.4	1.5	1.7	2.0	2.3	2.6	2.9	3.3
1.012	1.2	1.2	1.3	1.4	1.6	1.8	2.0	2.2	2.5	2.8	3.2	3.6
1.014	1.4	1.5	1.6	1.7	1.8	2.0	2.2	2.5	2.8	3.1	3.4	3.8
1.016	1.6	1.7	1.8	1.9	2.0	2.2	2.5	2.7	3.0	3.3	3.6	4.0
1.018	1.8	1.9	2.0	2.1	2.3	2.4	2.7	2.9	3.2	3.5	3.9	4.2
1.020	2.1	2.1	2.2	2.3	2.5	2.7	2.9	3.2	3.4	3.8	4.1	4.5
1.022	2.3	2.3	2.4	2.5	2.7	2.9	3.1	3.4	3.7	4.0	4.3	4.7
1.024	2.5	2.6	2.7	2.8	2.9	3.1	3.3	3.6	3.9	4.2	4.6	4.9
1.026	2.7	2.8	2.9	3.0	3.1	3.3	3.6	3.8	4.1	4.5	4.8	5.2
1.028	2.9	3.0	3.1	3.2	3.4	3.5	3.8	4.1	4.4	4.7	5.0	5.4
1.030	3.1	3.2	3.3	3.4	3.6	3.8	4.0	4.3	4.6	4.9	5.2	5.6
1.032	3.4	3.4	3.5	3.7	3.8	4.0	4.3	4.5	4.8	5.1	5.5	5.9
1.034	3.6	3.7	3.8	3.9	4.0	4.2	4.5	4.7	5.0	5.4	5.7	...
1.036	3.8	3.9	4.0	4.1	4.3	4.5	4.7	5.0	5.3	5.6	5.9	...
1.038	4.0	4.1	4.2	4.3	4.5	4.7	4.9	5.2	5.5	5.8	...	...
1.040	4.3	4.3	4.4	4.5	4.7	4.9	5.1	5.4	5.7	...	...	...
1.042	4.5	4.6	4.7	4.8	4.9	5.1	5.4	5.6	5.9	...	...	...
1.044	4.7	4.8	4.9	5.0	5.1	5.3	5.6	5.9	...	...	...	...
1.046	4.9	5.0	5.1	5.2	5.4	5.6	5.8	...	...	...	...	...
1.048	5.1	5.2	5.3	5.4	5.6	5.8	...	...	...	...	...	...
1.050	5.4	5.5	5.5	5.7	5.8	6.0	...	...	...	...	...	...

at the Forest Products Laboratory we have felt that it would be desirable to check this point in the case of zinc chloride solutions. Accordingly, the specific gravity of a 2.5 per cent and 3 per cent solution of



zinc chloride was determined at different temperatures. The data were published in the appendix of Forest Service Bulletin No. 126, in the form of tables and curves. It shows that for practical purposes the change in gravity of a 3 per cent solution of zinc



chloride is the same as a change in gravity of pure water over the same range of temperature.

The accompanying table and charts giving the strength of zinc chloride solutions may be of service to readers.

The table and the first chart give the specific gravity

of solutions ranging from 0 per cent to 6 per cent strength at temperatures ranging from 40° to 150° F.

The charts are used as follows: The specific gravity is determined by the use of a hydrometer and the temperature recorded by a thermometer.¹ After the specific gravity and temperatures are known the strength of the solution is found in the following manner: A horizontal line is drawn and the specific gravity recorded until it meets the oblique line marked with the temperature. The horizontal distance between the junction of these two lines and the left of the chart is a measure of the concentration. For example, the specific gravity at 90° F. was determined to be 1.025. The dotted lines on the curve show the method of using the chart. The strength of the solution taken as an example was 3.2 per cent, provided all of the dissolved material was zinc chloride. If this was not the case the strength of the zinc chloride solution was less than 3.2. The second chart shows the specific gravity of solutions of pure zinc chloride containing between 40 and 60 per cent of the chloride between 50° and 90° F. This curve is not plotted on so fine a scale, but it is believed that it is closer than the usual purity of zinc chloride used in wood preservative.

British Prices for Sulphate of Ammonia.

British manufacturers of sulphate of ammonia at a meeting last month decided to fix the following prices for home sales during the coming autumn and spring seasons for 24½ per cent quality for makers' works in makers' bags free:

To manure mixers, corn and manure merchants, 15s per cwt. net cash; to farmers, 15s 6d per cwt. net cash (3d per cwt. to be allowed if buyers supply bags). It was further resolved that, in order to encourage merchants and farmers to take early delivery, the following specially reduced prices should be fixed for quantities removed from sellers' works during the period August 1 to September 30, 1916: To manure mixers, corn and manure merchants, 14s 6d per cwt. net cash; to farmers, 15s per cwt. net cash, a condition of these sales being that quantities exceeding 15 tons be taken in equal monthly deliveries during August and September.

The U. S. Consul General at Christiania reports that a factory is to be erected at Greaker, Fredriksstad, for the utilization of refuse from sulphite. He states that a Swedish engineer has invented a method for extracting a substance from sulphite lye which, in powdered form, will be made into bricks and used as fuel. It is claimed that the powder thus formed yields 6,000 calories, while the best English coal gives 7,000. A company has experimented with the invention in Sweden and has produced a powder with nearly as much heating power as first-class coal.

¹The error introduced by the use of hydrometers at these temperatures is not great enough to materially affect the result in this case, and certainly are not as great as the error introduced by the solution containing materials other than zinc chloride.

ENGE AND OTHER FORMS OF' GROUNDWOOD.*

Additional particulars of the Enge process for the manufacture of groundwood pulp are given in a communication to the members of the Newsprint Manufacturers' Association issued on August 18. In submitting the new material, Mr. Steele says: "At various times in the past I have sent out from this office translations from foreign technical trade papers relating to new processes being experimented with abroad in the manufacture of groundwood pulp. Recently the interruption of foreign mails has prevented our receiving any mail from Germany. The last numbers of German trade publications which have been received are as follows: *Papier Zeitung*, No. 32, April 20, 1916; *Pappen Zeitung*, No. 11, March 9, 1916; *Papier-Markt*, December, 1915; *Papierfabrikant*, No. 10, March 10, 1916; *Neue Deutsche Papier Zeitung*, No. 3, March 10, 1916; *Wochenblatt für Papierfabrikation*, No. 15, April 15, 1916; *Zentralblatt*, No. 8, April 15, 1916."

Mr. Steele then enumerates a number of articles which he has had translated from the Norwegian on the new groundwood process. On March 2, 1916, he wrote to Leopold Enge, Petersdorf, Silesia, Germany, asking for definite information regarding the Enge process and for samples of the pulp and paper made from it. He received no reply, on account, perhaps, of the interruption of the mails from Germany to the United States. Those who are interested in the new experimental process of manufacturing mechanical pulp will peruse the accompanying articles with interest:

"NG" PULP AND OTHER GROUND FIBER PULP

A LECTURE TO THE TECHNOLOGICAL ASSOCIATION BY
CHIEF ENGINEER CHR. VIG.
(From *Papirjournalen*)

From the description of a patent and from the trade journals I have learned that a new method had been patented in Germany, the idea of which is treat the logs with hot water under pressure before the grinding process, to be treated afterwards in the customary manner in the grinder. I had read that from this pulp newsprint had been produced without any addition of cellulose. Through a business acquaintance, I got in touch with the inventor of the method, Leopold Enge, and it was soon agreed that it would be best if I paid him a visit so that I, as an eye-witness, could ascertain how the manufacturing was done. The trip there and back was about the same as in times of peace, except that the searching was more severe on the border, but the railways and ferries were just as punctual as at other times, and I did not notice any shortage of food, either in the restaurants or in the private families whose guest I was.

Mr. Enge has a paper mill in Petersdorf, in the Riesengebirge (East Germany), and in connection

with the paper mill he runs a little cellulose mill for his own demands. He has woodpulp mills at two falls higher up the river, and at the furthestmost one the wood to be ground is treated according to the new method. The wood is barked by hand, which in general is still the practice in this district; thereafter it is packed into a horizontal boiler having a capacity of 423.77 cubic feet and which is fitted with pipes for indirect heating.

When the wood had been packed, the digester was filled with water, previously heated in a boiler. Great care was taken that any air possibly enclosed should be let out through a valve. The water was heated to the desired temperature by direct steam influx, and when the water had reached the proper height (experiments were made with temperatures from 230° to 284° F.) the pressure pump was started and the pressure was brought up to a point which prevented the water from boiling. Now the temperature was maintained by the heating-coils inside the digester. The digester must be provided with the necessary apparatus for the measuring of pressure and temperature. The treatment lasted about three hours, and the wood when taken out was saturated with hot water. The higher the pressure and temperature, the more quickly the wood became saturated. The coal consumption was said to be about 44.09 lb. per 220.46 lb. dry pulp. I figure that the fuel value of 44.09 lb. of coal would correspond to 33.07 lb. of our small coal per ton of (2,204.62 lb.) 50 per cent woodpulp, and this was when cold water was used, that is, when the water was not used over again. In ordinary times, when the price of coal, for instance, is \$3.40 per short ton in the fire room, the treatment would cost in coal about .255 per short ton moist.

Wood treated in this manner was remarkably changed, inasmuch as it could be split the whole length through. The binding substance was plainly softened, and the chips were quite pliable. If the wood was left to dry for a time it became as before and the chips got stiff and brittle. This proves that the incrustations do not vanish in the treatment, but are merely softened. An observation by Mr. Enge indicates that the yield is greater from wood treated in this manner than from the same quantity of unboiled wood. The thoroughly boiled wood was ground on ordinary sandstone and screened by .039 to .043-inch perforations. The pulp when treated with water heated to 230° to 248° F. turned somewhat more yellow than ordinary pulp. At higher temperatures it assumes a rather strong brown, not so dark, however, as brown pulp. There could be ground per horsepower more of the "NG" than of the regular pulp. The pulp in form of sheets was very tough and permitted of stretching for yards in quite thin layers, this being the only way possible with fine tough pulp. On the paper machine it was easy to work without the addition of cellulose, the paper being solid, having a fine surface and a good "body." However, it was very slow, for which rea-

*From Paper.

son it was difficult to get the water drained off at great speed, but the paper machine, fortunately, was of an old type with few dryers, so it could not run faster than about 262.46 feet a minute, and at such a speed the draining of the water was satisfactorily effected. I was told that when this pulp was used there would not be any rosin spots on the wire.

In the Laboratory for Testing Materials, I have had tests made with regular newsprint paper and with paper containing only "NG" pulp. The result was:

	"N. G." pulp paper.	Ordinary newsprint paper.
Stretching	1.42 per cent	1.13 per cent
Breaking length	2,875 meters	2,789 meters
Number of foldings.....	3.1	9.8

The result shows that "NG" paper is somewhat stronger than ordinary newsprint, though it does not differ as much in the length and crosswise direction. But in the number of foldings, "NG" is absolutely inferior, as it reached on the average only 3.1, whereas the other could stand 9.8. I do not know if, as a rule, Norwegian newsprint paper can stand as many foldings. I do not think so. This result may be inconclusive and I will have more tests made. Anyhow, I have seen comparative tests made with German newsprint paper in which "NG" proved best with an average of 2.4 and 3.15 foldings, whereas newsprint paper containing cellulose, on the average, stood only 1.5, 2.7 and 1.13 foldings.

Mr. Enge is continuing his experiments. A couple of days ago I had a letter from him, dated March 9, in which he says: "However, it has been stated at a mill that the power consumption for grinding of saturated wood was 36.2 horsepower per net ton of pulp in 24 hours.* The grinding method most suitable for this wood has not yet been fully ascertained. I have found that I am getting more pulp with high pressure and little water than otherwise. You yourself are grinding this way, I presume. For screening I have found it possible to use perforations up to .059 to .063 inch to 1.6 mm. On the other hand, I will not recommend the use of coarser stones; stick to those now used. In the boiling of the wood I am getting the best results in the following manner: The water, within the shortest time possible, is brought up to 266° F. and the steam is shut off totally. My injector brings the pressure up to 176.36 pounds per square inch and with the pressure pump the pressure is kept on 176.36 pounds per square inch during about three hours. In this time the temperature will fall about 59 degrees F., but this will do no harm. In that manner the wood remains whiter than when steam is permitted to flow all the time, even if it is indirect."

Nevertheless, when it is a question of getting long fibers, efforts should be made to grind the wood in such a manner that the fibers are not destroyed; therefore, fibers should not simply be cut off. By the

ordinary method of grinding, the wood is pressed onto the stone so that the sand grains—which each by itself may be regarded as a knife—cut the fibers off crosswise. In this manner the fibers are not obtained at their utmost length, because even if the fibers are treated with hot water, so that they are loosened, many of them will not be torn loose but cut over by the sand grains, and in the most lucky instances only partly damaged. If the fibers remain full length, the wood has to be ground in the lengthwise direction of the fibers. This is known from old times, but as the production is much less in lengthwise grinding, this method has long ago been abandoned. It does not pay when wages are high and power expensive. The thing that is obstructing production is that the stone happens to work against the wood, and the pulp clogs between the stone and the wood.

Engineer Andersen, in Hellefos, for a long time has been experimenting with modified lengthwise grinding. He places the logs at an angle of about 10 degrees against the stone, and then gets a fiber of considerable length, which is fine and pliable, almost resembling cellulose fiber. Mr. Andersen reports that the production is greater than in regular grinding; the grinding method can be adapted to old grinding machines and the necessary changes required will cost but a trifle. To those mills which use their pulp, an improvement of the pulp will mean a great saving, because then they can do with less cellulose. To wood-pulp mills which sell the pulp, the advantage is, that by an arrangement, requiring but a small expense, they will get a pulp better than warm ground pulp, and therefore more valuable, getting, moreover, an increased production. A combination of both these methods of treatment, with hot water and angle grinding, perhaps will prove ideal, and this will be tested at one of the Union Company's mills as soon as the machinery has been installed. The angle grinding, as mentioned before, has been in use for some time at Hellefos.

"LENGTHWISE" GRINDING.

A CRITICISM BY H. T. MELBYE.

Engineers Vig and Andersen have patented a modified form of so called lengthwise grinding of wood, which is also discussed in the *Papirjournalen*. Lengthwise grinding is an old system, which was discarded because the log was subjected to the grinding action of the stone in its middle division only, with the result that both ends of the log were untouched and fell off. Moreover, the stone worked against the grain and the grinding surface became so large that the water could not penetrate, and the pores in the sandstone became clogged with pulp, the production being much reduced in consequence. In Germany it was sought to overcome these obstacles by using three stones, mounted one after the other and grinding the log in great lengths. This was given a to and fro movement (Freitag's patent). Later only one stone

*This would correspond to 15.98 short tons per HP. annually, and is almost 50 per cent more than the regular.

was used and the grinding box was given a reciprocating sidewise movement (Schmidt's patent). With the patent of Vig and Andersen this movement is avoided but otherwise the principle is the same.

BOTH QUALITY AND QUANTITY OF PULP DEPEND ON THE GRINDING ANGLE

In regard to lengthwise grinding it may be of interest to recall, says H. T. Melbye, of Labro, Norway, that the Labro woodpulp mill in the beginning of the "eighties" changed to this method, but the change did not bring the results looked for and after a few years' experience it was found necessary, even with great economic sacrifices to return to crosswise or oblique grinding. However, practice had taught that a considerably better quality was obtained than formerly and that quality as well as quantity was dependent on the grinding angle. In 1896 Professor Kirchner made measurements in regard to the production from lengthwise grinding which showed a comparison to diagonal and crosswise grinding of 1:2.5. The conditions, in this case, may have been unfortunate for the lengthwise grinding, but at any rate it is indisputable that lengthwise grinding with large grinding surfaces is very irrational. That the production, according to this new method, should be greater than from ordinary cross grinding is therefore not very likely and concerning this further exact statements are much to be desired. That there should be obtained any significant increase in the production because the angle deviates 10 degrees from the radial cannot be accepted offhand. The test by Professor Kirchner proves nevertheless also that for the amount of production it is of extremely little importance if the pressure is radial or somewhat deviating therefrom. (See Kirchner: *Die Holzstofffabrikation*, pages 95-97.)

So far as I know, there have been no experiments made in the country on a large scale with lengthwise grinding, probably for the reason that the commercial woodpulp mills have not found it economical to grind a really good quality of pulp.

As a rule the papermakers have always succeeded in depressing the price for prime pulp so that the difference between this and the ordinary pulp has become nominal and is not nearly corresponding to the extra expenses which are combined with quality grinding.

By and by as competition grew livelier, the commercial woodpulp mills were forced to change to the simplest possible method, with but few and powerful grinding machines and high pressure, and by producing an even, good, medium quality the production has been increased, the cost of production being correspondingly reduced. A change to the new method would signify a change to quality grinding, and from earlier experiences there is but little hope that the papermakers would be willing to pay the additional cost, which the pulp in fact is worth, or the increased expenses which the woodpulp mills surely would have to meet by grinding the fibers lengthwise. For the

present, therefore, it is likely that the grinding of this excellent quality can only be a question for such mills as use the pulp themselves. The additional cost of the new method, if my contentions prove to be correct, will no doubt be apparent on all sides, the production per horsepower will be less, more machinery for screening will be needed, more powerful pressures, and there will be increased labor expenses, not only because the log has to be cut into small lengths but also because the filling of the grinding boxes is made more difficult and the log will more easily clog than heretofore. A combination of the Enge patent and the method of Vig and Andersen may possibly prove satisfactory, and by a combination of this kind it is likely that some of the objections raised might be removed.

ANGULAR WOODGRINDING.

In subsequent issues of the *Papirjournalen* communications are made by Engineers Vig and Andersen as follows:

THE YIELD IN ANGULAR GRINDING.

I.

Regarding the yield from the stone used for angular grinding, Engineer Vig says:

"Replying to H. T. Melbye's article in the last number of the *Papirjournalen*, I would state that the yield from the stone which was used for angular grinding is figured from the amount of wood consumed, as there was no reason under ordinary conditions to keep the pulp separate. However, experiments with angular grinding will now be made in several places; at one pulp mill it will be used all over the whole plant and I will then be able to get exact statements of the quantity produced per horsepower a day. So far it has not seemed as if more machinery would be needed for angular grinding than for ordinary grinding, and the quality of the pulp is changed less by dressing than in crosswise grinding, therefore the quantity of the ground pulp to be treated is pretty much alike.

"That there is a demand for a longfibred pulp has been amply proven by later developments, seeing that more pulp mills have been rebuilt for warm grinding. A woodpulp which can be used for paper without, or at any rate with very little, cellulose added, will bring a better price than a woodpulp which needs a large addition of cellulose. Cellulose prices are so high at present that papermakers will be glad to pay an extra price for a woodpulp which permits a reduction in the cellulose percentage."

II.

Engineer N. A. Andersen, of Hellefos, Norway, describes experiments in the production of mechanical pulp by the patented lengthwise grinding process. He says:

"In accordance with the request of Engineer Melbye in the *Papirjournalen*, I will consent to give some information regarding my experiments with lengthwise grinding.

"At the first experiment there was used an ordi-

nary grinding stone for crosswise grinding 70 in. by 26 in. with a power consumption of 250 hp. The pressure was 141 pounds on a 6-inch cylinder and the surface of wood exposed to the stone measured 286 square inches. The grinding angle was 10 degrees.

"For dressing there were used from seven cuts to the inch down to five cuts, without any real change in quality and quantity being observed. It became evident to me that it depended on the coarseness of grain of the stone and I put in a quite coarse brownstone and then I obtained a quite different result: big yield, an excellent pulp not too greasy, but strong and with long fibers.

"The angle in which the wood is placed against the stone does not influence the yield so much, it is more the quality; because the greater the angle, the shorter are the fibers, and wood ground at an angle of 45 degrees will yield only flour.

"The pulp which was shown at the last meeting of the Technical Association of the Papermakers, and which was marked A-B, was ground on brown stone dressed with seven and five cuts to the inch.

"The reason why lengthwise grinding formerly did not give better results was that the experiments were made with too fine stones and too little pressure on the wood, and that the wood was placed at too great an angle against the stone.

"There is one drawback to this method and it is that the wood has to be cut so short, but the resulting waste is counterbalanced by the fact that there is less waste from the stone. When the wood is placed angularly against the stone there will be formed a wedge, and this wedge will in the grinding decrease backwards and disappear without any further waste, grinding chips being in this way avoided. There will also be less loss in the screens, as this pulp is long fibered and does not contain so much flour, which was ascertained by microscopic tests. The work of cutting will be facilitated by using a gangsaw, so that two logs may be cut instead of one.

"The refining will be the same if a drum is used.

"Then it is said that the grinding men will constitute an added expense. This, I think could be so arranged that one man could be placed on every shift to pile the wood around the stone, so that the grinder men might be free to attend to the stones properly.

"The screening of pulp ground lengthwise should be made by .512 inch perforated plates and the pulp water ought to be somewhat more diluted than ordinarily, and if the screens are not too heavily loaded, it should hardly need any changes therein.

"Pulp made according to this method should be suitable for the manufacture of newsprint paper, as it is longfibered and strong.

"Probably the cellulose percentage can be considerably reduced and that is the main thing.

"In using finer stones, it will be possible to produce any kind of specialty pulp, but this would result in a lessened yield and might therefore become a ques-

tion of price. The pulp should command a higher price for the manufacture of newsprint because it requires less sulphite and produces a better paper than ordinary groundwood."

REVIEW OF GRINDING PROCESSES.

The closing contributions to the *Papirjournalen* articles on grinding processes were by Director P. Ebbinghaus, of Copenhagen, who reports the results of two experiments, as follows:

DIAGONAL GRINDING.

"In the eighties I had an opportunity to try the machines for diagonal grinding in the Priem woodpulp mills on the Chiemsee river. The apparatus was so arranged that the stones had a to and fro movement. The pulp produced was of an unusually smooth and cottonlike nature; nor was it necessary to cut the stones as frequently as in ordinary crosswise grinding. Unfortunately, it happened too often that the stones burst, as well as other disturbances in the run, so that, after some time, it was found expedient to return to the old method with stationary stones.

LENGTHWISE GRINDING.

"As one of the first grinding experts, I once introduced lengthwise grinding in the woodpulp mill in Bavaria, which I managed; the pulp was very highly approved, especially by the makers of printing paper. The reason we started this grinding method chiefly was that we had received tobacco stems from a big tobacco stems, which were to be defibrated by grinding. In order to get really long and fine fibers, we chose the lengthwise grinding method, by which the tobacco was defibrated between the log and the stone. The result, however, was not favorable for making cigarette mill, which were to be defibrated by grinding which made it very suitable for other purposes. To my regret I had to give up lengthwise grinding because the yield from my soft, fine ground Grillenburg stones was too small and the wear on the stones proportionately too large. In that respect, Engineer A. N. Andersen certainly had the right idea when saying: 'I was convinced immediately that it was the grain of the stone that was effective. A quite coarse brownstone gave a large yield and excellent pulp.'

"I did not comprehend this, and in mine, as well as in many other German woodpulp mills, the new method unfortunately was totally abandoned.

"Mr. Andersen has thus stated that the grain of the stone in lengthwise grinding is the basis for economical production. In this connection I cannot lay too much stress on the great advantages which artificial stones offer in lengthwise grinding as compared to natural stones. Among them it is easier to find the most suitable grain and the quality of stone most suitable for the grinding process. The future of the Andersen method in my opinion is also closely connected with the development in the manufacture of artificial stones. In the first place the Hercules stones from Saxony, and the Norrena stones from Norway will come under consideration.

"Further I would recommend that thorough experiments be made with diagonal grinding, and with coarser grain than those recently used. Maybe it would be well if the method was developed so that the work was done as warm as possible, and with the stone immersed deep in the pulp.

"Should these suggestions influence further experiments with the Andersen grinding theory, an excellent result in my opinion will be unquestionable, and the purpose of this article would then have been attained."

DYE PRODUCTION IN GREAT BRITAIN.

The annual report of the directors of British Dyes, Ltd., indicates the rapid development of the British dye industry under the stimulus of war demand.

The issued share and loan capital consisted as at Aug. 1, 1916, of: Share capital subscribed (864,179 shares of £1 each, 10s per share called up), £864,179; loan from Government, £1,064,179—total, £1,928,358. Since the date of the report submitted to the statutory meeting of the company, July 5, 1915, the subscribed share capital has increased by £208,080 and the loan to which the company is entitled from the Government has increased by £209,629, making together an increase of £417,709.

The board has established: (1) a committee of directors, which gives continuous attention to the affairs of the company; (2) a technical committee, which combines the heads of the technical and scientific departments, with Dr. Forster as chairman; (3) a research department, of which Professor W. H. Perkin is the head. On account of the delay and expense which would have been involved in erecting during the war a central research laboratory, it has been arranged that in the meantime the research work, so far as not conducted in the works laboratories, should be carried on in the laboratories of different universities, under the supervision of the professors of organic chemistry. Research colonies have been established in this way, employing a number of assistants, under the respective professors, and much important work is being carried out; (4) an advisory council, which consists of twelve eminent professors of chemistry connected with different universities, in addition to the members of the technical committee.

Notwithstanding the restriction caused by the shortage of certain materials owing to the war, the supply of dyes from the company's works has been greatly increased. A new plant has been erected and is in course of erection for further increasing the supply of those dyes which are most in demand and which can be made in large quantities from the materials available. In the near future the supply will be further substantially augmented. The company has also sent to the Swiss manufacturers considerable quantities of raw materials and intermediate products, without which they would not have been able to continue their supplies to the British markets.

A report from Mr. Turner, the manager of the company's works, in regard to the supply of dyes is appended to the directors' report. A committee appointed by the Board of Trade has made an exhaustive inquiry into the color requirements of this country. Mr. Turner, who represents this company on the committee, has, with the authority of the board of directors, submitted proposals for the prevention of overlapping in manufacture and for utilizing the resources of all dye makers in the country to the fullest advantage.

After conferring with a number of the leading users of dyes the directors decided, so far as the new works are concerned, to provide, in the first place, mainly for manufacturing on a large scale, raw materials and intermediate products. They desire to call particular attention to two important considerations: (1) In order to secure a permanent national supply of dyes, it is imperative that the manufacture of the intermediates from which dyes are made should be successfully established in the country; (2) the production of these intermediates requires the operation of a series of processes not hitherto worked on a commercial scale in Britain and it also requires complicated and expensive plant. A large amount of research and experimental work has been done, and a considerable quantity of plant has already been erected for the production of intermediates. Other important plants are in course of construction, including plants for paranitraniline and betanaphthol. As regards raw materials, the benzol and phenol plant has been largely increased. An acid plant, sufficient for the company's requirements, is approaching completion, and a large part of it is in operation.

As the result of conferences with a commission specially appointed by the French Government, the board has adjusted a provisional agreement with Le Syndicat National des Matieres Colorantes (a national company which has been formed in France with the support of the French Government. This agreement provides for a complete exchange of knowledge and processes, and for the formation of an inter-allied company to establish co-operation between the two companies in regard to the production of intermediates and dyes.

According to preliminary statistics prepared by the United States Bureau of the Census, the cotton consumed in the United States during August, 1916, amounted to 558,717 running bales (counting round as half bales) compared with 464,392 bales in the corresponding month of 1915. The quantity for 12 months ending July 31, 1916, was 6,397,613 bales compared with 5,597,362 for the corresponding period last year. Cotton on hand August 31 in the United States in consuming establishments amounted to 1,359,380 bales, compared with 1,105,681 a year ago; and in public storage and at compresses, 969,304 bales compared with 1,712,504 bales a year ago.

THE SECOND NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES.

The Second National Exposition of Chemical Industries, which is to be held at the Grand Central Palace, New York City, during the week of Sept. 25, promises to be the chief industrial event of the year. Already every one of the 275 exhibit spaces at the exposition has been taken. To meet the requirements of the societies who will hold meetings at the Grand Central Palace the auditorium has had to be increased in size, so that now it will comfortably seat 500 persons. An automatic motion picture machine of the latest design will be used to display the motion pictures, many of which will be loaned by exhibitors. In many cases there will be lectures to take the audience through a pictorial tour of a plant and they will be shown machinery and processes in the manufacture of materials that, until then, had never been previously shown. Many of the films are at present being made and are expected to be finished in time to be shown at the exposition. A few of these films are as follows:

- Making of black powder.
- Manufacture of iron.
- Manufacture of fertilizers.
- Mining and manufacturing of iron.
- Manufacturing of silk.
- Making of blotting paper.
- Silver mining.
- Manufacturing of Varnish.
- Asphalt.

Two other features of the exposition that have been added this year are a large section showing the opportunities that await the chemist in our south and known as the "Southern Opportunity" Section and a section for the "Paper and Pulp Industry" composed of materials and machinery used in the manufacture of paper and other related products.

The "Southern Opportunity" Section is an ambitious undertaking to display to our chemists, chemical engineers and capitalists the great latent wealth that awaits them in the undeveloped resources of the south. Not only will it show them these resources but will forcibly bring to their attention the debt they owe their country in return for the education and knowledge gained in its institutions of learning. It will show that the materials have formerly been shipped to foreign countries to be enhanced in value by manufacture and returned to the original producers at a greater price. Let efficiency enter and inefficiency pass!

The Bureau of Mines is preparing an elaborate exhibit that will cover much space—it will be a working exhibit, one where the visitor can see the "wheels go round"—every one wants to see that.

The exposition—a product of the chemist and by chemists, will be opened by chemists—Dr. Charles H. Herty, president of the American Chemical Society and chairman of the Exposition Advisory Committee, will make the opening address. Mr. Francis A. J. Fitzgerald, president of the American Electrochemical

Society, and Arthur B. Daniels, president of American Paper and Pulp Association, will also make addresses, after which the assembled guests will visit the exhibits.

The American Chemical Society whose annual meeting is being held during the week and in conjunction with the exposition, have arranged for conference meetings that will take the nature of symposiums—they will be industrial in nature and be engaged in by captains of industry—leaders in the field of the industry under discussion.

Other meetings of the society will be held at Columbia University, at the College of the City of New York and the Chemists' Club.

The Chemists' Club, who will also have a headquarters at the exposition, have offered the lobby of the club house for the registration of the members of the society. The Chemists' Club, which is a few squares from the Grand Central Palace, has been selected as the headquarters of the American Chemical Society, and on Monday afternoon the council of the American Chemical Society will hold a business meeting there, followed by a dinner tendered to the council by the New York Section.

The American Electrochemical Society has arranged a series of very interesting meetings beginning on Thursday morning, September 28, with the "Made in America" technical session at the Grand Central Palace. This session will be devoted to papers and discussions on the great and varied electrochemical industries of America. This will be followed on Friday morning by another technical session, devoted to the theoretical side of electrochemistry. Registration will be held on Wednesday evening at the exposition. Headquarters of the Electrochemical Society will be at the Electrochemical Society booth at the exposition.

The Technical Association of Pulp and Paper Industry who are also holding meetings in conjunction with the exposition, are arranging their headquarters in the midst of the "Paper and Pulp Industry" Section on the second floor of the Grand Central Palace. A large number of interesting papers are promised on the technical aspects of Pulp and Paper Manufacture. On Friday morning the meeting will be held in the auditorium at the Grand Central Palace, and the afternoon meeting will be a joint conference with the American Chemical Society.

The members of the American Chemical Society and the American Electrochemical Society, who register with their societies, will receive badges—these will admit them to the exposition without further tickets.

The U. S. Geological Survey, Department of the Interior, now has available for distribution its annual statement on Salt, Bromine and Calcium Chloride in 1915. Increases are recorded in the production of all three of these substances during the year.

BRITISH PRODUCTION OF SYNTHETIC ORGANIC DRUGS.

In a paper read before a recent congress of the British Society of Chemical Industry, Francis H. Carr, F. I. C., discussed at length the effects produced in that country by the scarcity of synthetic drugs due to the war for the reason that such important lines as anti-pyrim, aspirin, salicylic acid, phenacetin, chloral hydrate, salol, phenyl salicylate, saccharin, veronal, sulphonal, trional, eucaine and novocaine were not manufactured in Great Britain, and the total import of this class of products was over a million pounds annually. With war conditions difficulties of production increased enormously, but these have been to a great extent surmounted. The author detailed some of the considerations which must face future production. The German power is largely chemical power. Salvarsan is a powerful illustration of England's dependence upon Germany before the war, but the immediate intervention of one large firm in England, and of another in France, saved the situation.

"As to the future," he said, "some form of protection is of vital necessity to our chemical industry, for without it anything accomplished will be demolished rapidly and completely by competition from abroad." The author exemplified this by mentioning the recent combination of German dye and chemical manufacturers to meet opposition after the war, and he said that Germany will recognize English successful prosecution of chemical industry to be of greater material importance than the recovery of lost colonies and European territory. He also submitted that no opportunity should be lost of impressing upon the nation and its rulers the fact that the possession of a powerful and self-contained chemical industry is of the same degree of importance as a great engineering industry has proved to be. Educational requirements and grants are only the initiation of the work. Something more must be done to safeguard new industries. He instanced the synthetic production of camphor in England as an example of the way not to do things. That new industry was abandoned by the pioneers, with serious loss of money, when the state might have saved the situation by encouraging the manufacturers in some way.

"German competitors will adopt a variety of skillful maneuvers," the speaker asserted, "to combat the new developments in Great Britain, such as charging high prices for immediate products, offering low terms for finished products on long-period contracts, systematic dumping, etc. In this connection the absence from the Board of Trade committees of any dealing with the chemical industries he held to be ominous. Mr. Carr considered that an immediate decision to extend for a period after the declaration of peace the pro-

hibition against the importation of German chemicals would have a far-reaching effect by giving confidence to capitalist enterprise."

As to the manufacture of synthetic drugs he considered that this will be determined by the dye-industry, which can ensure the supply of intermediates required in manufacturing medicines, artificial perfumes and photographic chemicals. He pointed out some of the plant that will be available, such as that of the new coke ovens, and speaking with reference to other necessary articles he said:

"So badly are we placed in this country with regard to supply of cheap alcohols, acetone and acetic acid, and so important are these to this country in time of war and to chemical industry at all times, that some action should be taken to promote industrial research in these connections. Cheap and pure methyl and ethyl alcohols lie at the very foundation of fine-chemical manufacture. No other one obstacle has barred our progress in this industry so much as the government restrictions on their use. In the synthesis of organic compounds methyl and ethyl alcohols are daily necessities, and must be used in large quantities. The restrictions make industrial methylated alcohol dear, while the impurities added for methylating are a constant source of trouble. If the authorities remove the duty from pure methyl alcohol (or shall we call it carbinol to obviate official confusion?) and allow pure methyl alcohol (as an effective ear-mark) to be used in denaturing, nearly all difficulties will be overcome."

German Potash Output.

A Berlin dispatch under date of Aug. 25 states at a meeting of the German potash syndicate the president announced that business during the first seven months of 1916 amounted to 103,000,000 marks. This sum compares with a total of 70,500,000 marks for the similar period in 1915 and 113,000,000 marks for the first seven months in 1914.

New works according to a daily Commerce Report are about to be started at Drammen for the extraction of zinc by an electric wet process, invented by a Belgian engineer. Raw materials for the first year, about 10,000 tons, have been secured, and special attention will be paid to ores containing from 8 to 30 per cent zinc, which have hitherto been considered worthless.

The statement on Platinum and Allied Metals, issued annually by the Geological Survey, Department of the Interior, is now available for 1915. The production of crude platinum from California and Oregon during the year was 741.91 troy ounces, having a value of about \$23,500.

NEW CUBAN SUGAR PLANTS.

The U. S. Consul at Habana, Cuba under date of Aug. 26, reports that as an indication of the prosperity and rapid expansion of the sugar industry of Cuba, it is now announced that there will be 16 new mills grinding in the crop of 1916. The names of these new centrals and the probable output of each this year are:

Name of central.	Location. (Town and province.)	Owners.	Estimated output, in sacks.
Adelaida	Moron (Camaguey)	Laureano Falla Gutierrez	50,000
Occidente	Quivicán (Habana)	Galdos, Tarafa y Linares	40,000
Hershey	Santa Cruz del Norte (Habana)	Hershey & Co.	100,000
Galope	San Juan y Martinez (Pinar del Rio)	Cia. Azucarera Central Galope	25,000
Baragua	Colorado (Camaguey)		50,000
Nombré de Dios	Guines (Habana)	Ignacio Pla	30,000
Virginia	Los Palacios (Pinar del Rio)	Cia. Azucarera Cubana	30,000
Oriente	Javier (Oriente)	Marcane, Gil y Chibas	80,000
Tacajo	Alto Cedro (Oriente)		40,000
Alto Cedro	Marcane (Oriente)	Alto Cedro Sugar Co.	50,000
Miranda	Palmarito (Oriente)	Cia. Azucarera Miranda	50,000
Santo Tomas	Moron (Camaguey)	Del Campo y Cia.	50,000
Van Horne	San Jenaro (Camaguey)	Cuba Co.	70,000
Cunagua	Moron (Camaguey)	Antonio Mendoza	30,000
Algodones	Guayacanés (Camaguey)		11,000
Punta Alegre	Punta Alegre (Camaguey)	Atkins, Stone & Co.	150,000

It will be noted that the estimated output of these new mills approaches 1,000,000 sacks (320 lbs. each). The machinery and equipment of the new centrals will in the main be the product of the United States.

THE CHEMIST AND THE FOOD INDUSTRY.*

By DR. H. E. BARNARD,†

One of the largest and most successful canners and packers in the country recently said to me: "I have been packing foods for thirty years, and I have felt that I knew all there was to know about the business, but I have made up my mind that I really don't know anything about it, and I am putting in a laboratory that I may learn what I am doing."

His statement, or confession, is a good illustration of the present viewpoint of the food manufacturer. Fifteen years ago the young chemist either turned to teaching or looked for work in some fertilizer factory. Very few chemists found an opportunity for work in the food industry, and what little investigation was carried on was for the most part done from time to time by the consulting chemist, who never came in close touch with the industry.

With the passage of State and Federal legislation, and especially the latter, the food industry was confronted with the appalling fact that it could not continue in business unless it produced goods that complied with the laws and standards, and since the arbiter of the law is the chemist whose analyses determine purity or adulteration, the demand for the work of a chemist who could keep products up to standard

was largely increased. The success of these chemists has been surprisingly great.

As the chemists got in close touch with their industries they saw always opportunities for improvement in quality, reduction of waste, regulation in the purchasing of supplies; indeed, they made their services invaluable.

Laboratories starting in with one analytical chemist

now have half a dozen, and the analyst has been succeeded by the chemical engineer, whose work is not confined to the routine of the laboratory table, but who in a large measure is responsible for the operation of the factory.

As the lawyer is employed in drawing up papers of incorporation, investigating titles, and determining legal points, so the chemist is the technical adviser of the manufacturer on all points having to do with the food laws, and his responsibility is so great that his services have been more and more appreciated.

Chemists, in well equipped laboratories supplied with every convenience of apparatus and officered by competent assistants, are actually revolutionizing the methods and the products of their industries.

Look back to the condition of the canning factory five or six years ago, a business developed in the majority of cases by the importunities of salesmen of canning factory material and apparatus, carried on by the co-operative organizations of farmers who had absolutely no training in their work, and whose success or failure as canners depended upon their ability to sell their output at a slight advance over the cost of production. Knowing nothing of sanitation, moulds, yeast spores or bacteria the product of the factory was so prone to spoilage that preservatives were used to supplement imperfect sterilization. And when preservatives were forbidden witness the chaotic condition into which the industry was thrown. Now every canning factory, indeed every food factory, finds it absolutely necessary to employ an expert whose daily reports pass or condemn the product.

The chemist has come into his own. The astonishing development of his field of work is but an indication of what the future will offer.

*From a paper read at the recent convention of the Food Commissioners at Detroit.

†President of Chemists' Section of Food Officials' Association.

PRICES OF CHEMICALS, OILS, ETC., SEPTEMBER, 1916

WHOLESALE PRICES PREVAILING IN NEW YORK MARKET ON SEPTEMBER 15

CHEMICALS, INORGANIC.

Acetate of lime, 100 lbs.	\$ 5.00 @ 5.05
Alum, ammonia, crystals, lb.	.05 @ .
Aluminium sulphate, 100 lbs.	.04 @ .04½
Arsenic, white, lb.	.06 @ .06¾
Barium chloride, ton.	110.00 @ 115.00
Barium nitrate, kegs, lb.	.14 @ .15
Bleaching powder, drums, 100 lbs.	4.00 @ 4.50
Blue vitriol, car lots, 100 lbs.	9.50 @ 10.00
Bine vitriol, powdered, 100 lbs.	14.00 @ 16.00
Borax, car lots, f. o. b., N. Y., 100 lbs.	7.50 @ 8.00
Brimstone, crude, ton.	35.00 @ .
Caustic soda, 74 to 76%, lb.	.02¾ @ .04
Chalk, precipitated, cases, lb.	.06 @ .06½
Glauber's salt, bags, 100 lbs.	.60 @ .65
Nitric acid, 36 to 42°, 100 lbs.	7.50 @ 8.00
Phosphoric acid, 1.750, lb.	.30 @ .34½
Potassium bichromate, lb.	.39 @ .40
Potassium carbonate, calcined, 90 to 96%, lb.	.80 @ .90
Potassium chlorate, crystals, lb.	.46 @ .47
Potassium cyanide, bulk, 100 lbs.	.45 @ .50
Quicksilver, flasks	75.00 @ .
Silver nitrate, ounce.	.42¾ @ .44¾
Soda ash, 48%, car lots, 1917 contracts, 100 lbs.	1.25 @ .
Sodium acetate, lb.	.14 @ .15
Sodium bicarbonate, American, 100 lbs.	1.65 @ 2.00
Sodium bichromate, lb.	.28½ @ .30
Sodium chlorate, 100 lbs.	.30 @ .35
Sodium hyposulphite, in bbls, 100 lbs.	2.00 @ 2.25
Sodium nitrite, lb.	.12 @ .14
Sodium sulphide, crystals, 100 lbs.	2.50 @ 3.00
Sulphuric acid, 60° and up, cwt.	1.50 @ 2.00
Sulphuric acid, 60°, ton.	30.00 @ 35.00
Talc, domestic, spot, ton.	15.40 @ .
Tin bichloride, 50°, 100 lbs.	13.50 @ .
Tin oxide, lb.	.43 @ .45
Zinc oxide, lb.	.11 @ .15

CHEMICALS, ORGANIC.

Acetanilid, lb.	.65 @ .70
Acetic acid, 28%, 100 lbs.	4.80 @ 5.00
Acetic acid, glacial, 99½% carboys, lb.	.32 @ .36
Acetone, drums, lb.	.30 @ .31
Alcohol, denatured, 188 proof, gal.	.55 @ .56
Alcohol, grain, 188 proof, gal.	2.68 @ 2.70
Alcohol, wood, 95%, gal.	.65 @ .
Amyl acetate, gal.	4.75 @ 5.00
Benzoic acid, from tuluol, cwt.	11.00 @ 12.00
Carbolic acid, drums, crystals, lb.	.55 @ .60
Carbon, tetrachloride, lb.	.17 @ .20
Chloroform, lb.	.50 @ .55
Citric acid, domestic, crystals, lb.	.67 @ .67½
Cresole, U. S. P., gal.	.75 @ .80
Ether, U. S. P., 1900, lb.	.15 @ .20
Formaldehyde, 10%, carboys, lb.	.11½ @ .12
Glycerine, dynamite, lb.	.42¾ @ .45
Pyrogalllic acid, crystal, lb.	2.90 @ 3.20
Salicylic acid, lb.	1.75 @ .
Tannic acid, technical, lb.	.90 @ 1.01
Tartaric acid, crystals, U. S. P., lb.	.60 @ .66¾

DYE MATERIALS.

Acid orange, lb.	1.75 @ 4.00
Aniline oil, drums, imported, lb.	. @ .
Aniline, domestic, lb.	.30 @ .35
Aniline (white), gal.	.70 @ .75
Bismarck brown, lb.	2.25 @ 2.85

Carmine, lb.	4.70 @ 5.00
Cochineal, silver, lb.	.75 @ .80
Cochineal, black, lb.	.73 @ .75
Gambier, lb.	.09½ @ .10.
Indigo, madras, lb.	.03 @ 1.00
Logwood extract, 51°, lb.	.25 @ .28
Madder Dutch, lb.	.21 @ .23
Methyl, violet, lb.	9.00 @ 15.00
Methylene, technical, lb.	7.00 @ 10.00
Prussian blue, soluble, lb.	1.35 @ 1.50
Sulphur, black, lb.	1.30 @ 1.90
Sulphur, brown, lb.	.50 @ .60
Zinc dust, prime to heavy, lb.	.25 @ .30
Zinc oxide, American, lb.	.11 @ .12
Zinc sulphate, lb.	.07½ @ .08

ESSENTIAL OILS.

Almonds, bitter, lb.	12.50 @ 14.00
Amber, crude, lb.	1.25 @ 1.50
Anise, technical, lb.	1.05 @ 1.10
Camphor, Japanese, 72 lb. cans, lb.	.16 @ .20
Cinnamon, lb.	19.00 @ 20.00
Clove, lb.	1.20 @ 1.25
Cubeb, lb.	3.25 @ .
Ginger, lb.	5.50 @ 6.50
Limes, distilled, lb.	2.75 @ 3.00
Pennyroyal, prime, American, lb.	1.65 @ 1.85
Peppermint, prime, American, lb.	2.25 @ 2.40
Spearmint, oz.	1.75 @ 2.00
Wintergreen, synthetic, oz.	1.75 @ 1.85
Wormwood, oz.	2.85 @ 3.00

FERTILIZER MATERIALS.

Ammonium sulphate, 100 lbs.	3.60 @ 3.65
Blood, dried, N. Y., 100 lbs.	2.95 @ .
Blood, dried, f. o. b. Chicago, 100 lbs.	2.50 @ .
Bone black, sugar discard, ton.	27.00 @ 30.00
Bone, oil discard, ton.	18.00 @ 20.00
Muriate of potash, 80-85%, ton.	300.00 @ 350.00
Phosphate, acid, per unit, ton.	80.00 @ 96.00
Sulphate of potash, 90%, ton.	275.00 @ .
Tankage, Chicago, 100 lbs.	2.50 @ .

OILS.

Castor oil, No. 3 bbls., lb.	.13½ @ .
Corn oil, crude, 100 lbs.	7.75 @ 7.85
Corn oil, refined, 100 lbs.	8.91 @ 8.96
Cylinder oil, light filtered, gal.	.26 @ .30
Cylinder oil, dark filtered, gal.	.19 @ .20
Fusel oil, refined, gal.	5.50 @ 6.00
Linseed oil, carlots, gal.	.72 @ .
Menhaden oil, crude, Southern, gal.	.48 @ .49
Naphtha, auto, 68@72°, gal.	.37¼ @ .36¾
Paraffine oil, high viscosity, gal.	.20½ @ .30
Soya oil in bbls, lb.	.07¾ @ .08
Spindle oil, No. 1, gal.	.19 @ .20
Spindle oil, 20 gravity, gal.	.17 @ .18
Tar oil, commercial, gal.	.25 @ .27
Turpentine, gal.	.43¾ @ .44

WAXES, ETC.

Beeswax, ordinary, pure, lb.	.32 @ .36
Ceresin wax, yellow, lb.	.10 @ .30
Ceresin wax, white, lb.	.14 @ .40
Japan wax, lb.	.14 @ .14½
Paraffine, crude, 124-126 mp., lb.	.05¼ @ .05¾
Pitch, pine, first grade, bbl.	4.75 @ .
Rosin, B grade, N. Y., bbl.	6.30 @ 6.35
Stearic acid, lb.	.11 @ .13½
Tar retort, bbl.	7.25 @ 7.75

NOTES OF CHEMICAL AND ALLIED INDUSTRIES.

Air Products.—The Linde Air Products Co., 42d St. Bldg., New York City, has received bids for the construction of a 1-story 100x100 ft. factory at Minneapolis, Minn., to cost about \$40,000.

Alloy Steel.—The Toledo Alloy Steel Co., of Toledo, O., has been incorporated with a capital stock of \$75,000 and proposes to manufacture alloy steel. For the present the company's product will be produced by the Boerder Process Steel Co. E. R. Hiatt is interested.

Beet Sugar.—The Great Western Sugar Co. has awarded contracts for the construction of two beet sugar factories, one at Brighton, Colo., the other at Missoula, Mont. It is planned to have both plants completed in time to handle the 1917 crop. The plant at Brighton will cost \$1,500,000 and that in Montana \$1,250,000. Both factories will be equipped with facilities for drying the beet pulp, to make it more valuable as feed for stock, the Brighton plant being the first one in Colorado to be so equipped. The Brighton plant will have a capacity of 1,200 tons of beets every 24 hours, and the capacity of the Montana plant will be 1,000 tons of beets a day. The Larrowe Construction Co. of Detroit secured the contract for the factory and the machinery at Brighton and for the machinery for the Missoula plant.

Beverage.—The Anheuser-Busch Brewing Association, St. Louis, Mo., has awarded contracts for a \$2,500,000 plant for the manufacture of a new non-intoxicating beverage. The building will be 7-story, 250x580 ft.

Chemicals.—The Whitcombe Chemical Co., Inc., Batavia, N. Y., has been organized under the laws of this state with a capital stock of \$200,000. Incorporators, W. S. Whitcombe, 406 East Main St.; J. W. Couplan, 56 Pearl St., Batavia, N. Y.; J. H. Haelber, 12 Faradam St., Rochester, N. Y.

Chemicals.—The Atlantic Chemical Co. has been organized at Portland, Me., with \$200,000 capital, by M. B. Phipps, H. F. Pierce and H. P. Sweetser.

Chemicals.—The Mifflin Chemical Corp., Philadelphia, Pa., has been incorporated with a capital stock of \$100,000 and proposes to engage in the manufacture of chemicals. David Berg, 1715 Jefferson St., Philadelphia, Pa., is interested.

Chemicals.—S. Wander & Sons Chemical Co., 75 Church St., Albany, N. Y., propose the construction of a factory 3-story, 127x70x100 ft. in size, to cost \$70,000.

Chemicals.—Frederick Post Co., Chicago, has awarded a contract for a \$10,000 addition to its chemical factory at Chicago.

Chemicals.—The Morano Chemical Works, 1800 South 2d St., St. Louis, Mo., has awarded a contract to the Kellerman Construction Co., St. Louis, for a 1-story, 50x60 ft. addition to its factory. Widman

& Walsh, Wainwright Bldg., St. Louis, are the architects.

Chemicals.—The Falico Chemical Co. of St. Louis, Mo., has been incorporated with a capital stock of \$25,000 and proposes to manufacture chemicals for coatings of metal, wood, etc. Spencer C. Graves and William Stephenson are interested.

Chlorine.—The Electrolytic Chlorine Co. of Guthrie, Okla., has been chartered with a capital stock of \$10,000. J. M. Williams is interested.

Drugs.—F. W. Simpson, 11 Merchants' Bank Bldg., Aurora, Ill., has started construction on alterations to his drug manufacturing factory at Downers Grove, Ill.

Dyes.—A company has been formed at Decatur, Ala., for the purpose of manufacturing dyes by a secret process. It is stated the ingredients used for the dyes are obtained from waste matter from large factories. A patent on the dyes has been asked for in the United States and will be applied for in other countries later. Jack F. Dilehay, New Decatur, Ala., is Secretary and Treasurer of the company.

Dyes.—The Gulf Reduction Co. of Pensacola, Fla., has been chartered with a capital stock of \$30,000 and will engage in the manufacture of dyes. J. H. D'Alemberte is President and J. A. Wright, Secretary and Treasurer.

Dyestuffs.—The International Dye Co. of Milwaukee, Wis., has been incorporated with a capital stock of \$30,000 and will engage in the manufacture of chemicals, dyestuffs, etc. William F. Rudolph and August Oesterreich are incorporators.

Explosives.—An expenditure of \$100,000 is to be made by the American Explosive Co. for installing equipment for the manufacture of dynamite near Sarcoxie, Mo. The plant will have a capacity of 30,000 lbs. per day. George W. Qualls, Carthage, Mo., and A. B. McAbee, Pittsburgh, Pa., are interested.

Fabrikoid.—The Dn Pont Fabrikoid Co., 864 Dufferin St., Toronto, Ont., will erect a \$150,000 factory at Toronto.

Glass.—The Whitney Glass Works Charles Y. Yost, Secretary, Bullitt Bldg., Philadelphia, Pa., will enlarge its plant at Glassboro, N. J., by the construction of a new factory to occupy an entire city block. It will be 264x411 ft., and is expected to be ready for operation in about six months. The building will be one story, of brick, steel and concrete.

Glass.—A. H. Heisey & Co., Newark, O., have awarded a contract to W. B. Patton, Newark, for a 3-story, 50x110 ft. addition to its factory.

Glass.—Western Flint-Glass Co. of Checotah, Okla., has been incorporated with a capital stock of \$15,000. Geo. J. Miller and T. G. McDaniel are interested.

Metal Castings.—The Falco Chemical Co., St. Louis, Mo., has been incorporated with a capital stock of \$25,000 by Guy N. Hitchcock, William Stephenson and Spencer C. Graves and will manufacture coatings for metals, wood, etc.

Molybdenum.—The International Molybdenum Co., J. L. Murray, President, proposes equipping an electrically operated refining plant at Renfrew, Ont., at a cost of \$150,000.

Leather.—The Union Tanning Co., New York City has purchased the plant of the American Oak & Leather Co., at Harriman, Tenn.

Leather.—The Ashland Leather Co., Ashland, Ky., has awarded the contract to Central Engineering Co., Charleston, W. Va., for a 2-story, 250 ft. by 75 ft. reinforced concrete extension to its yard building, that will increase the capacity 50 per cent. The estimated cost of the improvement is \$70,000.

Leather.—The Wilmington Leather Co., Wilmington, Del., has had plans prepared for a \$50,000 factory. James O'Neill, Webb and Greenhill Ave., Wilmington, is in charge.

Paint Product.—Construction is underway on the plant at St. Louis, Mo., for the Mineral Refining & Chemical Corp., Railway Exchange Bldg., St. Louis. The company has a capital stock of \$1,500,000 and will install plant having daily capacity 50 tons product based on zinc as a substitute for white lead and zinc oxide in paint manufacture.

Paper.—Lewis F. Haupt of Buffalo, N. Y., President of the George Irish Paper Co. of Buffalo, and the Monarch Paper Co. of Toronto, has purchased the Thompson Paper Mills at Newburg, Ont. The buildings are being repaired and the latest machinery will be installed for the manufacture of high grade bond paper. George B. Thompson will be resident manager of the plant, which will be ready for operation by Nov. 1.

Paper.—Northern Board & Paper Co., Sumner, Wash., has awarded a contract to H. D. Stewart, American Bank Bldg., Seattle, Wash., for constructing a \$40,000 addition to its plant.

Paper.—A contract has been awarded by the Thompson Norris Co., 355 Notre Dame St., E., Montreal, Que., for the construction of a reinforced concrete and brick paper factory and power house to cost \$84,000. Lockwood & Greene, Boston, Mass., are the architects.

Paper.—The Toronto Paper Mfg. Co., Cornwall, Ont., of which W. Wallace is manager, will install additional machinery to bring the capacity of its plant up to 30 tons per day.

Paper.—Frank Hill Co., Dayton, O., has been awarded contract for extensive additions to plant of Mead Pulp & Paper Co., on First St., Dayton.

Paper.—Terre Haute Paper Co., Terre Haute, Ind., will expend about \$300,000 for the building of an additional plant.

Paper.—The Hawley Pulp & Paper Co., Enterprise, Ore., probably will begin construction about Jan. 1 on the second additional unit to its paper mills. The completed plant will have a daily capacity of 50 tons of paper and will cost \$1,000,000.

Paper.—W. H. Crocker of Old North State Pulp & Paper Co., Wilmington, N. C., has plans under construction for constructing a mill of 50 tons daily paper capacity. The plan includes the purchase of 30,000 acres of land.

Potash.—Plans are reported in progress for a \$150,000 potash factory to be constructed in Southern California for the U. S. Government. C. W. Brown, Bureau of Soil Agricultural Department, Washington, D. C., is reported in charge.

Pulp.—Financial arrangements are understood to have been completed by George F. Whelan, for the opening of pulp mills at Quatsino Sound, and Swanson Bay, Ontario, in addition to the present works of the company at Howe Sound. A new plant will be opened at Swanson Bay with a capacity of 30 tons of sulphite fibre daily. At Quatsino Sound a production of 120 tons daily will be handled by the Colonial Pulp & Paper Mill, a \$2,500,000 corporation. In the new works upward of 1,000 men will be employed.

Silk.—The Merrill Silk Co., Hornell, N. Y., will establish a branch plant in Dunkirk, N. Y. An improvement company has been formed for the construction of a factory, which is to be leased for a long term of years by the silk company. The plant will be of brick and steel construction and fireproof throughout. William West has been elected president of the improvement company and William T. Madigan, Secretary. It is planned to start operations with 250 operatives.

Sugar.—Miller & Lux have closed leases for approximately 10,000 acres of land at Buttonwillow and Conners Station, California, to be devoted to sugar beet culture. The crops of beets will be sold to the San Joaquin Valley Sugar Co. It is tentatively planned that Bakersfield, Cal., as the sugar beet harvests enlarge, shall become the location of a sugar factory.

Sugar.—A certified copy of the articles of incorporation of the Pingree Sugar Co. have been filed with the County Clerk at Hanford, Cal. The Corcoran sugar factory was recently purchased by this company. The articles state that the company is capitalized at \$1,000,000, and its chief center for manufacturing is Tulare County. The life of the company is 50 years, and the directors are George T. Crandall, Alameda; R. R. Nickerson, Berkeley, and J. W. Wasson, Oakland.

Sugar.—The People's Sugar Co., incorporated on Aug. 20, with a capital stock of \$765,000, will at once begin the construction of a sugar factory in Sanpete County, Utah. The company already is understood to have 4,500 acres of land under 3-year contracts for beet raising. N. G. Stringham, Salt Lake City, Utah, is Secretary of the company.

Sugar.—The United Fruit Co., 131 State St., Boston, Mass., will expend \$2,000,000 for the construction of a sugar refinery plant near Boston, Mass. The plant will consist of six buildings, one of 9 stories, the others 5-story and 8-story. The general contract has been let to the H. P. Converse Co., 88 Broad St., Boston, Mass. William Higginson, 13 Park Row, New York City, is the architect, and Robert S. Kent, 50 Church St., Brooklyn, N. Y., is the mechanical engineer.

Sulphite.—The Lincoln Paper Mills Co., Merrittton, Ont., proposes the construction of a sulphite plant to cost \$200,000.

Sulphuric Acid.—The Fairmont Chemical Co., Fairmont, W. Va., will erect on Tygart Valley River a sulphuric acid plant with a capacity of 10,000 tons per annum, to be operated by the Multiple-Tangent System. An auxiliary plant for the manufacture of nitric acid will also be erected. It is estimated the plant will cost from \$75,000 to \$85,000. The building will be constructed of steel and concrete and will be fireproof. The plans were by Ludwig A. Thiele, Columbus, Ohio, who will be the engineer in charge of construction.

Sulphuric Acid.—The Erie Chemical Works, Erie, Pa., a branch of the Franklin H. Kalbfleisch Co., 31 Union Square, New York City, is to enlarge its plant facilities. A new acid plant and a new office building are to be erected. The Erie plant manufactures sulphuric acid and alum.

Tannery.—The Merrill, Wis., plant of the Michigan Tannery & Extract Co., Petoskey, Mich., has been destroyed by fire with a loss of about \$100,000.

Tannery.—Plans have been completed for a \$1,000,000 tannery plant to be erected at Hartford, Ill., for the International Shoe Co., St. Louis, Mo. Shepard & Morgan, Edwardsville, Ill., are the architects and engineers.

Rubber.—The Pennsylvania Rubber Co., Inc., has been incorporated under the laws of New York, with an authorized capital of \$6,000,000, composed of \$5,000,000 of common stock and \$1,000,000 of 7 per cent cumulative preferred stock. The company will handle and care for the increased volume of business of the Pennsylvania Rubber Co. The directors chosen by the Pennsylvania Rubber Co., Inc., are Herbert DuPuy, H. Wilfred DuPuy, C. M. DuPuy, Seneca G. Lewis, George W. Shiveley and George A. McLaughlin.

Soda Ash.—The American Soda Products Co., Lakeview, Ore., made the first shipment of soda ash from Alkali lake the middle of August. The company is now installing machinery that will increase its output from 14 to 60 tons per day.

Tungsten.—Plans have been completed for a \$60,000 tungsten mill to be erected in Colorado for H. M. Byllesby & Co., Chicago, Ill.

Turpentine, etc.—The Calvert Turpentine & Rosin Co., of Calvert, Ala., has been chartered with an authorized capital stock of \$20,000 and proposes to manufacture turpentine oils, wood pulp, etc. G. W. Laubenthal is President and C. J. Laubenthal is Secretary-Treasurer.

Wood Extract.—The Federal Extract Co. has been organized at Bristol, Va., and proposes construction of a plant to manufacture wood extracts.

Wood Extract.—The Federal Extract Co., J. A. Newcombe, President, Bristol, Va., propose the erection of a plant to cost \$100,000 for the manufacture of chestnut wood extract.

Wood Extract.—H. E. Young & Co., Pittsburgh, Pa., are reported contemplating erection of a \$150,000 plant at Charlottesville, Va., for the manufacture of wood extracts.

Zinc.—National Zinc Works has awarded a contract to L. Crosby & Son, Kansas City, Mo., for interior remodeling of its factory at Argentine, Kan. The improvement will cost about \$25,000.

Feldspar.—Goldin Sons Co., J. M. Manor, manager, East Liverpool, O., has awarded a contract for the erection of a \$30,000 feldspar factory at East Liverpool.

New Chemical Companies Chartered in August.

New companies for the manufacture or distribution of dyestuffs, drugs or chemicals incorporated in August had a total capitalization of \$1,375,000. The total capitalization of similar companies incorporated in August, 1915, was \$3,260,000. These figures relate only to companies having a capital stock of \$100,000 or more. The grand total capitalization of these companies incorporated since Jan. 1, 1915, is \$126,118,000. The following table from the Journal of Commerce shows the incorporations during August and the state in which the charters were obtained:

Whitcombe Chemical Co., New York.....	\$ 200,000
Michigan By-Products Chemical Co., New York....	100,000
Atlantic Chemical Co., Maine.....	200,000
Cie Marcel, a corporation, manufacturing chemicals, New York.....	100,000
The White Tar Co., of N. J., manufacturing chemicals.....	50,000
Fore Chemical Works, Inc., Delaware.....	475,000
Basis Products Corp., Delaware.....	100,000
Phoenix Dye Product Corp., New York.....	150,000
Total	\$1,375,000

Chemical Engineer and Manufacturer

Vol. XXIV.

OCTOBER, 1916.

No. 4.

PUBLISHED MONTHLY by the MYRON C. CLARK
PUBLISHING CO.,

608 S. Dearborn Street, Chicago

*Entered as Second Class Matter, Aug. 19, 1907, at the Post Office
at Chicago, Illinois, under Act of March 3, 1879.*

Subscription—United States, Cuba and Mexico, \$2.00
Extra postage to Canada 25c a year; to foreign countries 50c a year.
Remittances may be made by check, draft or money order in favor of
CHEMICAL ENGINEER AND MANUFACTURER

All communications should be sent to CHEMICAL ENGINEER AND
MANUFACTURER, 608 S. Dearborn Street, Chicago, Ill.

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THE NEED OF MORE SCHOOLS TO TRAIN FOREMEN FOR OUR CHEMICAL INDUSTRIES.

Within the past 25 years, there has been created a growing demand from industries for young men with chemical training. As a result of this demand, many excellent chemical courses have been established in our universities and technical schools, the graduates from which have found a ready welcome in nearly every line of manufacturing. These young men, for the most part, have been employed as analytical chemists and, through hard work and untiring effort, have risen to positions of responsibility and trust. The demand for such men has been gradually increasing, until, at the present time, there is hardly a sufficient number available to meet the demands. As our manufacturing processes have become more complicated within recent years, there is another problem which confronts us—that is, the ability to handle these complicated processes in an intelligent manner in the works. In other words, we have come to realize that we must have not only research chemists to work out new processes, and technically trained men in our laboratories to test the materials purchased and the products manufactured, but likewise men in our plants to make these products who are also technically trained, that is to say, we must make provision for the training of our foremen. Many a process has been pronounced a failure, and many a product ruined, because unintelligent supervision was exercised during the preliminary trials.

That such a condition exists was felt by the trustees of Pratt Institute, and, as a result, in 1905, a course in applied chemistry was established, which has for its aim the training of young men for foremanship positions in our growing chemical industries. In selecting the one to take charge of the industrial phase of the work, the trustees made a very thorough canvass in order to secure a man who, through previous teachings and technical experience, would be qualified to develop the course along such lines as would best meet the requirements of our chemical industries. The man finally selected for the position was Dr. Allen Rogers, a graduate from the chemistry course of the University of Maine in 1897, an instructor in chemistry at that institution for three years; obtained his Ph. D. from the University of Pennsylvania in 1902; was a Senior Fellow at the same school for one year; was an instructor there in organic chemistry for one year; subsequently for one year was research chemist

for the Oakes Manufacturing Company, Long Island City.

In organizing the work Dr. Rogers attacked the problem from an entirely novel standpoint, as he believed that, to train men for factory work, it required that they have factory experience. It being impossible to put the student into actual factories, the next best method was adopted—that of building model factories at the school, where the student might handle materials on a sufficiently large scale to approach commercial conditions.

In the original plan, five model plants were selected, being a soap factory, paint factory, chemical works, dyeing equipment, and tannery. Since the inauguration of the course, however, the scope of the work has greatly enlarged; the equipment in all of the original plants has been materially increased, and several new plants have been installed, the latter being a dry-color and ink works, varnish equipment, and an intermediate and dyestuff plant. In working in these model plants, the students are assigned in groups, one of the members being foreman. The equipment is of such a character that the marketable products can be produced, and, being of a high standard, they find a ready sale. The returns from the sale of manufactured articles are sufficient to offset the cost of raw material. During the past year, the sales from these manufacturing plants, not counting the material used in the manufacture of other products or sold to other departments of the Institute, amounted to over \$2,500.

By working in the model plant, the student becomes familiar with the handling of machinery, gains experience in the control of men, and acquires confidence in his own ability to work with materials which have a money value. He also learns that to spoil a batch of goods means money lost, or to make an inferior article lowers the efficiency of his plant. In carrying on this work, the foreman must also keep a record of all operations, the cost of raw material, take into account the item of labor, wear and tear of machinery, cost of container, and interest on the investment.

The object of the course, as stated above, is to train foremen, and so the instruction is not treated as an engineering problem, the idea being simply to fit young men to handle practically every kind of a piece of apparatus and machine that is found in any chemical manufacturing plant.

Of course, it should be understood that the work in the industrial laboratory is only a part of the instruction given, other essential subjects being necessarily included. In conjunction with the practical work, Dr. Rogers discusses the important problems of the day, which, either from his personal experience in factory work or from his intimate knowledge as the author of several books on industrial chemistry, give the student first-hand information of conditions as they exist in the manufacturing plants at the present time.

Since the inauguration of the course, the number of applicants for admission has increased from 8 for the first year to over 140 in the past three years. As the number admitted is limited to 35, it is plain to see that more than 100 bright young men have to be disappointed each year. This may serve as food for thought for other schools, which might well consider offering courses along similar lines.

The question as to what becomes of the young men may be asked, and so it might be well to note that they are employed in nearly every line of industry. Of the 300 odd graduates, there are: managers, 11; assistant managers, 3; superintendents, 18; assistant superintendent, 31; foremen, 66; chief chemists, 16; chemists, 98; in other lines, 6, and out of employment, 1; the remainder being employed as inspectors, salesmen, or other workers connected with chemical industry.

As an outgrowth of the course in applied chemistry, and largely as a result of the efforts of Dr. Rogers, who is considered an authority on leather, courses in tanning and applied leather chemistry were opened at Pratt Institute in 1911. In conducting these courses, the Institute has the financial and moral support of the National Association of Tanners and the allied industries, as well as the hearty co-operation of all of the leather trade journals. The majority of students enrolled in these tanning courses come directly from the trades and, on completion of their course, usually return to the plant from which they came. Many plants even send their men and not only meet the expenses of the course but keep them on the payroll during the time.

The tanners of the country realized that the future of their industry depended upon having young men with technical training occupy the positions of responsibility in the plants, and so they appointed a committee and raised the necessary funds to meet the needs. They now realize that, in order to place the industry on a still higher plane, it will require the unhampered attention of the research chemist. To accomplish the higher aim, another fund is being raised, which will insure the establishment of a very complete research laboratory. This research work will be carried out in conjunction with the tanning course where the facilities of the best equipped tanning school plant in the world will be at the disposal of the research chemist and his staff. The National Association of Tanners, therefore, have done the wise thing by first seeing to it that they had technically trained men in their plants before starting a line of investigation which would eventually find its application in the tannery.

Other lines of industry may well profit by the experience of the leather industry, and, in doing so, help to make America the greatest manufacturing center of the world.

CHEMISTRY AND BANKING*

By JOHN E. GARDIN.†

The present struggle at arms sooner or later will be followed by a struggle, possibly just as fierce, for the supremacy of commercial interests, and in this the chemist will play no small part. At one time England held the whip hand and had absolute control over the chemical industry of the world. But this position has been wrested from her by the plodding and thrifty industrial methods of Germany, and the future necessity of each country standing on its own merits has been brought to the world's attention in a most forceful manner by the present conflict prevailing in Europe.

The familiar economic theory that things should be purchased where they can be produced the cheapest, while fundamentally sound, has, from the practical standpoint, disadvantages that become apparent only in times of stress and trouble. The people of the United States of America never before have realized how dependent they were upon the German chemist, not alone in the matter of dyes but also of other chemicals, and the sudden collapse of the commercial relationships between the two countries is a calamity.

The lesson has been taught us, and it now remains for the people of this country to profit by it. That they will do so, there is not the slightest doubt in my mind. But the great fear is that the attempt will be only a sporadic one and that, just as soon as the European equilibrium has been re-established, matters will again run along the lines of least resistance and, before we know it, we shall again be the vassals of some European power so far as certain industrial products are concerned.

Theoretically I never was a believer in tariffs, having been educated in a school where free trade was considered the acme of scientific government. Practice, however, teaches us a different lesson, and the cost of any other policy must be put to book in our national system, just as the cost of the upkeep of our military and naval service—and that is the protection of our natural resources. It is through the intervention of tariffs that the inequalities of methods of production are equalized, and while to some it may not seem wise statesmanship to have imposed an especially high duty on dyestuffs to take effect after the war, still our legislators are perhaps to be congratulated that they have used foresight in this respect.

The capital invested in the chemical industry in this country, not alone directly but indirectly, is something enormous, and unless we enter upon a campaign of preparedness now, we are likely to receive some very rude shocks when the other war—that is, the economic war of nations—is launched upon us.

Theorizing is all very well, but it does not take a

very astute mind to determine that if the flood gates are open for the influx of the world's products later on, a great deal of this capital will be absolutely wiped out, and it, therefore, behooves the banker, the merchant, and the professional man to put his best efforts behind the one thought at the present time, and that is, to create a stability in our production that will resist all attempts of the outsider to overcome.

The chemical industry of the United States is making wonderful strides. It has quadrupled its output since 1880, and doubled it since 1905.

The capital invested is over six times as much as in 1880, and more than double that of 1905. This relates to the group of products classed by the census, from which the above figures are quoted, as "general chemicals." The capital in 1880 was \$20,000,000, in 1910, \$115,000,000 and in 1915 approximately \$200,000,000, this estimate of capital for 1915 being based upon official figures of product of that year. The value of products turned out in 1880 was \$30,000,000 and in 1915 approximately \$158,000,000.

In addition to this there is a large group of products, many of them very important, classified by the census as "allied industries," including fertilizers, dyestuffs, explosives, essential oils, wood distillation, sulphuric and nitric acids, bone, carbon and lampblack, and paints and varnishes. The value of the output of these "allied industries" is much greater than that of the group classed distinctly as chemicals, having been in 1886 approximately \$72,000,000 and in 1915 \$400,000,000; the capital employed in 1880, \$57,000,000, and in 1915 approximately \$480,000,000.

This makes the grand total of output of the groups of manufactures classed by the census as "general chemicals" and "allied industries" about \$550,000,000 in 1914 (census of 1915), and the capital invested approximately \$700,000,000, the 1915 figures of capital being estimates based upon known figures of output in that year and also known figures of capital in 1910.

All of the foregoing statements regarding the figures of the 1915 census, and those which follow, are necessarily based upon preliminary returns thus far received from the census of 1915, and must, therefore, be regarded as subject to revision, and in some cases, especially as to capital employed in 1914, merely estimates, based upon stated value of output in 1914 and capital shown by the 1910 census.

Moreover, the figures of the various census years are not absolutely comparable. The first special report on the manufacture of chemicals and allied products issued by the Census Bureau was presented in 1880, covering the manufactures of 1879. This report, like those of succeeding censuses, covered the operation of establishments engaged in the manufacture of acids, sodas, potashes, alums, glycerine, dyestuffs, tanning materials, explosives, fertilizers, pigments, wood distillation, salts and certain elementary substances. In addition, the census of 1880 included

*Address delivered at the convention of the American Chemical Society, Sept. 25-30.

†National City Bank, New York.

in its figures of "chemicals and allied products" soap, candles, glucose and sulphur, while all of these were omitted in the subsequent censuses. In 1890, however, paint and varnish were added to the group of "chemicals and allied industries," and in 1900 essential oils and lampblack were also added. Thus the figures of total output and total capital for the various censuses are not absolutely comparable, though the fact that paints and varnishes were substituted in, 1890 for the groups, soap, candles, castor oil, glucose and sulphur, suggest that the changes are not sufficient to affect seriously the grand totals of products and capital employed running through the census records beginning in 1880. The capital figures for 1915 are in all cases estimates, but based upon census figures of production for that year, and the comparison of figures of capital with production in 1910 and earlier censuses.

Attention is especially called to the relation of capital employed to the value of output. The figures quoted are in all cases those of the census, except, as above indicated, that the 1915 figures are my own estimates based upon the census figures of output for that year. It will be noted that a comparison of the figures of capital employed and product turned out shows a steady growth in the amount of capital utilized in the production of a given value of output. In the group "general chemicals," the census figures show, for 1880, \$29,000,000 of capital and over \$38,000,000 worth of products turned out. The 1910 census shows \$155,000,000 of capital and only \$118,000,000 worth of products turned out. This increase in the amount of capital utilized in producing a dollar's worth of chemicals has been steady and consistent, as will be noted by comparing figures of capital and output for each as given by each census. In the allied industries, conditions are similar. In fact, this general rule applied in most of the manufacturing industries, the capital employed in all manufacturing being, according to the census figures in 1910, 35 times as much as in 1850, the value of manufactures only 23 times as much as in 1850.

It is, however, proper to add that the Census Bureau itself states frankly that its figures of capital employed in the manufacturing industries are far less reliable than those of the value of the output, but as approximately uniform practice has been followed in the collection of the figures of capital from census to census they are presumably worthy of attention in considering the relative growths of capital and output.

The production of chemicals and allied products is quite widely distributed, though occurring chiefly in the section east of the Mississippi.

Chemicals form an important factor in the foreign trade of the United States, both as to imports and exports. Prior to the war, imports of chemicals were largely in excess of exports, but the war has greatly increased the exportation of articles included in the general group "chemicals, drugs and dyes." The total

imports of chemicals, drugs and dyes has grown from \$48,000,000 in 1890 to \$70,000,000 in 1906, and \$109,000,000 in 1916. The exports of chemicals, drugs and dyes were in 1890 \$9,000,000, in 1906 \$19,000,000, in 1914, the year preceding the war, \$27,000,000, in 1915 \$40,000,000, and in 1916 \$124,000,000, all of the above figures of imports and exports being for the fiscal years ending June 30th.

The United States is apparently the world's largest importer of chemicals, the imports of Germany in 1913, the year prior to the war, being about \$75,000,000, Great Britain \$70,000,000 and France \$50,000,000. The exports of Germany for 1913 were \$140,000,000, Great Britain \$60,000,000 and France \$25,000,000. It is proper to add, however, that these figures are only approximations, because of the uncertainty as to the grouping of many articles which by certain countries are classed under the general head of chemicals, drugs and dyes, and by other countries otherwise classified.

Unfortunately the American banks have not the wide powers in connection with this particular industry, or in fact any other industrial undertaking, that the European banks have. The law forces the banks here to pursue merely a commercial business and it is perhaps well that it is so. The relationships between

PRODUCTION OF GENERAL CHEMICALS IN THE UNITED STATES AND CAPITAL EMPLOYED.

U. S. Census Figures.

Census of	Capital.	Product.	Employes Number.	Wages and Salaries.
1880.....	\$29,000,000	\$38,600,000	11,000	\$6,200,000
1890.....	55,000,000	59,400,000	17,100	10,100,000
1900.....	89,100,000	62,700,000	21,200	12,100,000
1905.....	96,600,000	75,200,000	22,600	14,800,000
1910.....	155,100,000	117,700,000	27,600	20,300,000
1915 (a).....	220,000,000 (a)	158,000,000	No data	No data

(a) Estimate based on stated value of product in 1915 and stated value of capital and product in 1910.

PRODUCTION OF GENERAL CHEMICALS AND ALLIED PRODUCTS AND CAPITAL EMPLOYED, 1880 TO 1915.

Allied products include fertilizers, explosives, dyestuffs, essential oils, wood distillates, sulphuric and nitric acids, carbon, bone and lampblack, and paints and varnishes.

	Capital.	Product.
1880.....	\$86,000,000	\$99,000,000
1890.....	180,000,000	125,000,000
1900.....	238,500,000	202,500,000
1905.....	324,100,000	281,000,000
1910.....	483,700,000	425,100,000
1915.....	700,000,000 (a)	550,000,000

(a) Estimate based on stated value of production in 1915 census and census figures of capital and product in 1910.

PRODUCTION OF FERTILIZERS, EXPLOSIVES AND PAINTS AND VARNISHES, AND CAPITAL EMPLOYED, 1880 TO 1915.

Year.	Fertilizers.		Explosives.	
	Capital.	Product.	Capital.	Product.
1880....	\$ 17,913,000	\$ 23,651,000	\$ 6,585,000	\$ 5,802,000
1890....	40,594,000	39,181,000	13,539,000	11,353,000
1900....	60,686,000	44,657,000	19,466,000	17,125,000
1905....	68,917,000	56,541,000	42,307,000	29,602,000
1910....	121,537,000	103,960,000	50,168,000	40,140,000
1915....	No data	168,388,000	No data	42,160,000

	Paints and Varnishes.	
	Capital.	Product.
1880.....	\$ 17,333,000	\$ 29,113,000
1890.....	45,318,000	54,234,000
1900.....	60,653,000	69,582,000
1905.....	75,486,000	90,840,000
1910.....	103,995,000	124,889,000
1915.....	No data	149,049,000

the banks and the public in this country are quite different from what they are abroad. In America the banks are supposed to be the custodians of their clients' money, whereas in Europe the general idea is that the banks are the investors of the public's money and oftentimes the public is not quite so fortunate in the choice of fiduciary. Therefore, in view of this known circumstance, when failure overcomes a bank, owing to bad investments, it is taken as a natural consequence and unless absolute fraud can be shown no particular odium attaches to the bank's officers. In this country, however, surrounded as we are with legal technicalities, the banks are not in a position to employ customers' money in founding industries of any kind. In fact the law prohibits specifically national banks from owning stock of any character whatsoever.

This does not, however, mean that capital is not available for industrial purposes. No meritorious undertaking is ever allowed to suffer for want of the necessary means to develop it. Capital is a greedy monster and seizes upon every opportunity whereby an increase can be expected and the attention of the investor of the United States today is directed in a great measure toward the development of the chemical industry and its allied branches.

Under the protection of the Government through its tariffs, numerous projects will be brought forward for the exploitation of this, that, or the other enterprise, some of them meritorious, others of no value whatsoever. It must be borne in mind that the investor will not trust his money to anything that is not absolutely certain and, this being the case, it is futile to endeavor to attract his attention to anything that does not possess absolute perfection.

Chemistry is out of its swaddling clothes, and while it has a great future in most lines, the experimental stage in a great measure has been past.

Chemistry goes into practically every feature of the world's industrial activity, no matter how lowly it may be, and to be able to command such enormous power in the control of the human requirements, it seems to me the chemist should be a proud individual. In the olden days the alchemists sought the easy means of the transmutation of metals. The modern chemist, through his skill, his industry, and his research, turns the basest product into glittering gold.

Numerous tests have been made by the U. S. Bureau of Standards in connection with an investigation to determine the effect of dry heat on the physical properties of the rubber insulation of wire. This work is being carried out in collaboration with the testing department of the Pennsylvania Railroad Co. and other laboratories identified with the American Society for Testing Materials, the object being to develop an accelerated test for insulated wire than will indicate the probable life of the wire insulation under normal service conditions.

CURRENT EFFICIENCIES IN NICKEL PLATING BATHS WITH ROTATING CATHODES.*

By F. C. MATHERS and E. G. STURDEVANT.

This paper shows that the low current efficiencies in nickel plating with rotating cathodes are due to impurities in the solution. The presence of anything that can lower the current efficiency will have a greater action for a shorter time in the bath with the rotating cathode than with a stationary cathode, because the stirring will bring the cathode in contact with more of the solution. Calhane and Gammage,¹ who first experimented with rotating cathodes in nickel baths, gave no explanation for the lower yields which were 12 per cent, in some cases, compared with 90 per cent using stationary cathodes.

Bennett, Kenny and Dugliss² formulated the theory that the rotation of the cathode prevented the formation over the cathode surface of an alkaline film of ammonium hydroxide which was necessary for a high yield. This theory is untenable as shown by the yields with stationary and with rotating cathodes, becoming practically equal in value with baths that are sufficiently pure.

In a more recent paper, Bennett, Rose and Tinkler³ advanced the theory that the free acid or the hydrogen ions in the baths was the cause of the low yields, and that the yield with the rotating cathode was lower than with the stationary one, because the acid or the hydrogen ions in the bath was more rapidly brought up to the cathode. This theory was based upon experiments in which the addition of ammonium hydroxide was found to increase the yields with both rotating and stationary cathodes, but the yields with the rotating cathodes were always lower except in one case. The addition of the ammonium hydroxide initially increased the yields somewhat, but continuous electrolysis or ageing produced further gradual increases in the yields with both rotating and stationary cathodes. This agrees with the theory that impurities which cause the low yields are gradually eliminated during electrolysis. If the lower yields which they obtained with the rotating cathodes were due to the more rapid bringing up of hydrogen ions, it follows that the addition of sufficient ammonium hydroxide should have eliminated the hydrogen ions and thus made the yields with both rotating and stationary cathodes the same. No such place was found. With larger amounts of ammonium hydroxide (10 cc. of 1:10 in 120 cc. of bath), the yields decreased with both stationary and rotating cathodes. If these experimenters had used larger volumes of solution, greater variations would have been found. As it was,

*Paper presented at the 30th General Meeting of the American Electrochemical Society, in New York City, Sept. 28-30, 1916.

¹J. Am. Chem. Soc., 29, 1268 (1907).

²Trans. Am. Electrochem. Soc., 25, 335 (1914). J. Phys. Chem., 18, 373 (1914).

³Trans. Am. Electrochem. Soc., 27, 339 (1915). J. Phys. Chem., 19, 564 (1915).

the 120 cc. of solution very soon became purified by the electrolysis.

MANIPULATION.

Each experimental bath contained 24 grams of nickel ammonium sulphate, 3 grams of nickel chloride and 300 cc. of water. The nickel ammonium sulphate was a commercial preparation, bought from a plating supply house. The nickel chloride was a Schuchardt preparation. Two anodes made of pieces of nickel, stripped from electrolytic cathodes, were used in each bath, one on each side of a beaker. The total exposed area of the two anodes (not counting the surfaces towards the beaker) was about 53 sq. cm. (8.2 sq. in.). The anodes were suspended by lead strips or wires. The stationary cathodes were made of sheet copper, and each had a total area of 50 sq. cm. (7.7 sq. in.). The moving cathode, a copper rod having a surface in the electrolyte of 9 sq. cm., was rotated 2,200 revolutions per minute. A current of 0.2 amp., which was used in each case, gave a current density of 0.4 amp. per sq. dcm. (3.7 amp. per sq. ft.) with the stationary cathode and 2.2 amp. per sq. dcm. (20.6 amp. per sq. ft.) with the rotating cathode. The use of a larger or a smaller current density was found to have a negligible influence within experimental errors. Each bath was run for one hour with a stationary cathode and then one hour with a rotating cathode, a deposit of about 0.22 gram of nickel being obtained in each case. A copper coulometer was run in series with each experiment. The bath was then electrolyzed continuously or aged with stationary electrodes and a current of 0.2 amp. until another quantitative determination was desired, at which time a run was made with the stationary and with the rotating cathode as before. In this way the determinations of the yields at intervals showed the effect of electrolysis on the elimination of the impurities in the bath. Since yields with stationary and rotating cathodes were run in each bath, any variation in the bath itself did not affect the comparison of the two values. The age of a bath in the following tables means the number of hours that the bath had been electrolyzed or aged at the time the determination was started.

Bath No.	Age in hours.	Current Efficiency—	
		Rotating cathode. Per Cent.	Stationary cathode. Per Cent.
1	0	76.4	89.4
	3	91.9	92.2
	15	90.5	92.9
2	0	77.6	91.9
	3	87.7	93.2
	15	91.0	95.6
3	0	79.6	92.6
	3	89.8	90.9
	15	92.6	93.5
4	0	93.4	94.9
	7	82.2	88.1
	7	87.1	94.9
5	23	97.6	98.6
	32	98.2	99.5
	0	84.5	92.4
6	17	97.2	98.7
	33	96.8	99.2
	60	96.5	99.2
6	0	86.3	92.7
	13	90.7	97.1
	35	96.4	100

66	95.5	99.4
0	84.2	90.2
17	91	98.7
59	97.2	100

ADDITION OF REAGENTS TO NEUTRALIZE THE ACIDITY IN THE BATHS.

Bath 1 was untreated, 2 was boiled with freshly precipitated nickel hydroxide for ten minutes, 3 was treated with 1 cc. of 1:10 ammonium hydroxide, an additional 1 cc. being added before each of the subsequent runs, making a total of 4 cc. for the final determination, 4, 5 and 6 contained 1, 3 and 5 per cent¹ of borax respectively, and 7 was boiled for ten minutes with nickel borate.

In all cases the yields gradually increased as the baths became older. On the same bath the yields were lower with the rotating than with the stationary cathode. The logical conclusion is that free acid is not the cause of the low yields, otherwise these neutralizing substances, having removed the free acid, would have made the yields on the initial runs as high as after hours of electrolysis. Moreover, the addition of 2 cc. of 1:10 ammonium hydroxide just before electrolysis lowered the yields to 86.4 per cent (s) and 76.9 per cent (r) yet the bath was alkaline to litmus. It should be noted that the baths containing the borax very rapidly increased in efficiency during ageing. The gradual increase in yields with ageing is easily explained by the assumption that the impurities causing the low yields were gradually eliminated during the electrolysis. If free acid had been causing the trouble the yields would have gradually increased just as they did, the acid being exhausted during the electrolysis, yet the idea is unreasonable that any free acid could have been present in the baths after treatment with the neutralizing agents that were used. Apparently the nickel salts used in this work contained very little free acid, as is shown by the yields from the untreated bath being practically equal to those from the neutralized baths. The authors were unable to obtain bright adherent deposits from solutions containing 5 cc. or 10 cc. of 1:10 ammonium hydroxide, although Bennett and others show curves from these alkaline baths. It is well known that good nickel deposits cannot be obtained from baths that are alkaline to litmus.

TEST OF THE EFFICIENCY OF NICKEL HYDROXIDE IN NEUTRALIZING FREE ACID IN THE BATH.

Two baths that had been aged until high yields had been obtained were treated with sulphuric acid, which immediately lowered the yields. The baths were then boiled for ten minutes with nickel hydroxide, filtered and cooled. They then gave almost the same high yields that they did before the addition of the sulphuric acid. This showed that the nickel hydroxide completely neutralized the free sulphuric acid. The conclusion follows that a low yield in any bath which has been boiled with nickel hydroxide is caused by something other than free mineral acid. Moreover,

¹Per cent. in this paper means grams per 100 cc.

the data show that the yields immediately start at a high value if the impurities in the bath have once been removed. The data on the two baths are as follows:

Treatment of bath.	Current efficiencies in per cent. in bath with		No boric acid.	
	5 per cent boric acid.	Stationary.	Rotating.	Stationary.
Yield after ageing but before addition of sulphuric acid	98.6	96.2	98.	95.3
After adding 25 drops of concentrated sulphuric acid	76.9	58.9	62.9	55.9
After boiling for 10 min. with nickel hydroxide and filtering	96.9	93.7	98.5	96.9

The boric acid in some way prevented the yield from immediately returning to the value that was obtained before the addition of the sulphuric acid.

ADDITION OF BORIC ACID.

The baths were boiled with nickel hydroxide to neutralize any free acid, and were filtered before the boric acid was added.

Per cent of boric acid.	Age.	—Current efficiency in per cent.—	
		Stationary cathode.	Rotating cathode.
1	0	90.1	82.6
1	9	95.6	90.8
1	36	97.4	91.7
1	68	99.1	98.7
2	0	92.3	79.7
2	20	98.0	95.4
2	36	98.4	96.9
3	0	91.4	81.1
3	35	95.9	81.2
3	57	98.0	95.3
3	77	98.3	95.5
4	0	87.1	80.3
4	32	95.6	94.5
4	79	95.7	95.6
4	110	94.4	90.8

These data show that the free boric acid decreased the yields in a marked degree only when a concentration of 5 per cent or more was used. In all cases the yields gradually increased as electrolysis continued. Boric acid is weakly dissociated, hence it would not be expected to reduce the yields like a mineral acid.

ADDITION OF IMPURITIES TO THE BATHS.

Iron.—All nickel anodes contain iron as an impurity in quantities varying from 8 per cent in the cast nickel anodes to almost traces in the electrolytic cathodes which were used in these experiments. Any decrease in the yield produced by the iron is the result of oxidation by the air to ferric, with later reduction at the cathode to ferrous. If the iron which dissolves from the anodes as ferrous remained in this condition and was deposited as such, any effect on the yield would be practically negligible because the electrochemical equivalents of nickel and ferrous, 29.3 and 27.9 respectively, are so nearly the same. A bath to which 2 per cent of ferrous sulphate was added gave yields of 93.6 (s) and 86.9 (r) for the initial determination. The yields increased to 99.7 (s) and 97.1 (r) after continuous electrolysis for 94 hours. The cathodes were dark in color and contained much iron. With 4 per cent ferrous sulphate, the yields started lower,

83.7 (s) and 46.7 (r) and decreased to 48.9 (s) and 40.2 (r) after 43 hours. A large quantity of precipitate formed in the bath which probably became acid as a result of the hydrolysis. The first cathode contained 39 per cent of iron.

The addition of 0.33 per cent of ferrous ammonium sulphate to a bath that had been aged until yields of 96.3 (s) and 93.2 (r) were obtained, immediately lowered the yields to 91.4 (s) and 81.1 (r). The salts used in making a bath contained iron equivalent to 0.02 gm. of ferric ammonium sulphate, hence only a small portion of the reduction in yield in a regular bath can be attributed to the iron in the salts used or in the pure electrolytic nickel anode material. The iron in ferro-nickel anodes is sufficient to reduce the yields in stirred solutions where the conditions for oxidation are favorable.

Nitrates.—The addition of 0.05 gm. of potassium nitrate to a bath that had been aged until it was giving yields of 99.9 (s) and 97.2 (r) lowered the yields as follows:

Age.	—Current efficiencies—	
	Rotating.	Stationary.
0	76.2	88.7
4	88.5	91.5
9	89.0	94.1

The analysis of the nickel chloride used in this work showed nitrate equivalent to 0.025 gm. of potassium nitrate in 3 gm. of the nickel chloride, the quantity used in a bath. Only traces of nitrate were found in the nickel ammonium sulphate. These results show that nitrate is the impurity that is responsible for a large part of the initial depression in the current yields.

Organic Salts.—Ammonium citrate and ammonium acetate each produced a lowering of the yields as shown by the following tables:

Per cent of ammonium acetate.	Per cent of ammonium citrate.	Age.	Current efficiencies in per cent.	
			Stationary cathode.	Rotating cathode.
1	0	0	83.8	91.8
1	1	20	77.2	88.2
1	1	40	50.0	79.0
1	1	58	50.8	83.8
3	0	0	81.9	88.5
3	18	18	59.9	82.8
3	34	34	81.9	87.7
3	80	80	75.1	85.0
5	0	0	60.4	81.5
5	20	20	72.6	85.5
5	52	52	79.7	84.3
5	80	80	63.3	77.6
1	0	0	92.1	91.7
1	8	8	94.6	95.4
1	12	12	94.9	95.2
1	20	20	96.1	96.4
2	0	0	88.3	93.8
2	8	8	95.0	97.7
2	12	12	96.3	96.0
2	20	20	86.9	99.0
4	0	0	62.3	82.8
4	8	8	81.3	89.3
4	12	12	76.2	90.0
4	20	20	79.6	90.1

The baths with the ammonium citrate finally became alkaline during the course of the electrolysis, which accounts for the low results finally reached. Very small amounts of these organic salts did not produce appreciable lowering of the yields, hence it is thought

that the traces of organic matter² in the nickel salts contributed only slightly to the lowering of the yields.

BATHS PREPARED FROM PURIFIED SALTS.

Baths prepared from purified salts gave initially high yields. The nickel ammonium sulphate was prepared by three crystallizations of the salt obtained from some old baths that had been aged until high yields were obtained. The nickel chloride was purified by electrolyzing a solution of nickel chloride with electrolytic nickel anodes for fifty hours. The nickel chloride from this solution was then crystallized twice. The nickel chloride which seemed to contain most of the harmful impurities was the most difficult salt to purify on account of its great solubility. Potassium chloride (C. P.) in place of the nickel chloride gave high yields. The following table shows the results:

—Per cent—			Current efficiency in per cent	
Nickel chloride.	Potassium chloride.	Age.	Rotating cathode.	Stationary cathode.
3		0	96.0	96.5
3		15	96.3	99.1
3		30	96.9	99.0
	3	0	96.1	97.6
	3	15	98.2	98.8
	3	30	98.2	99.4

The increase in yields from these baths as ageing progressed showed that the salts were not entirely pure. Also the higher yields from the potassium chloride bath showed that it was purer than the nickel chloride.

VOLUME EFFECT.

It has been observed³ that the larger the volume of the electrolyte in silver coulometers, the heavier the deposit of silver. This "volume effect" was shown⁴ to be due to impurities by the fact that the weight of deposit was independent of the volume if the electrolyte was sufficiently pure. This gives an excellent method of demonstrating the effect of impurities on the efficiency of nickel deposition. Three nickel baths of 100, 200 and 300 cc. were prepared from the same salts and in exactly the same way. These baths were electrolyzed continuously with rotating cathodes and the deposits were weighed each hour. The data are as follows:

Age.	—Efficiencies in per cent—					
	—100 cc. bath—		—200 cc. bath—		—300 cc. bath—	
	Rotat- ing.	Sta- tionary.	Rotat- ing.	Sta- tionary.	Rotat- ing.	Sta- tionary.
0	85.8		83.3		74.2	
1	94.2		92.8		87.9	
2	97.8		93.4		91.1	
3	97.8				95.0	
4		96.9	97.5			
5			97.6			
6				97.3		96.5

The data show that it required about twice as long for the 200 cc. bath and almost three times as long for the 300 cc. bath to reach an efficiency of 97.8 as in the case of the 100 cc. bath. The area between each curve and a line parallel to the abscissa at 97.6 per cent was 1.82, 3.59 and 6.82 respectively for the 100,

200 and 300 cc. baths. These numbers, which represent the total depression of the efficiencies by the impurities in each bath, should stand in the same ratio as the volumes of the baths, which they do approximately. A determination, made with a stationary cathode as soon as the efficiency had reached 97.6 per cent, gave a result in every case equal within experimental error to the efficiency with a rotating cathode. This shows conclusively that any difference between the two must be due to impurities and not to any specific action of the rotation or agitation of the solution.

An additional confirmation of the theory was obtained by repeating the above experiments with 100, 200 and 300 cc. baths prepared from purified salts. The current efficiencies in all of them for the first hour were approximately the same, 98 per cent. This shows that there is a volume effect only when impurities are present.

The continuous electrolysis with rotating cathodes removed the impurities quicker than with stationary cathodes. Some impurities remained in a bath even after many hours of electrolysis with a stationary cathode, hence a rotating cathode in such a bath gave a lower yield than with a stationary cathode, because the agitation of the solution brought the remaining impurities to the cathode. It was not feasible to age all of the baths with rotating cathodes hence in most of the tables the stationary cathodes show the higher values.

SUMMARY.

This paper shows that the impurities in the nickel salts are the cause of the low initial current yields with stationary cathodes and the still lower yields with rotating cathodes. The following points are brought out:

1. Free mineral acid can produce this lowering of the yields, but the neutralization of the baths by boiling with nickel hydroxide did not overcome the trouble.
2. The yields from baths electrolyzed continuously with rotating cathodes started low but reached values of about 97.6 per cent in 2, 4 and 5 hours respectively for baths of 100, 200 and 300 cc. made from commercial nickel salts. Similar baths made from purified salts gave yields of about 98 per cent for the first hour regardless of the volume. This shows that impurities produce all the lowering of the yields.
3. The yields with stationary and with rotating cathodes are approximately equal in all cases where the baths are sufficiently pure. Nitrate lowered the yields more than any other impurity that was tried. Ferric salts, ammonium citrate or ammonium acetate lowered the yields, but ferrous sulphate up to 2 per cent was almost without effect.
4. Free boric acid lowers the yields somewhat when present in quantities greater than 2 per cent.

²Calhane and Gammage (1) reported organic matter as one of the impurities in nickel ammonium sulphate.

³Rayleigh, Phil. Trans., 175, 431 (1884).

⁴Rosa, Vinal and McDaniel, Bull. Bur. Std., 9, 516 (1913).

THE BUREAU OF MINES METHOD FOR
MEASURING THE VISCOSITY OF VERY
VISCIOUS SUBSTANCES, SUCH AS
HEAVY OILS, PETROLEUMS, AS-
PHALTS, RESINS, ETC.*

Bureau of Mines Technical Paper 157. "A Method for Measuring the Viscosity of Blast-Furnace Slags at High Temperatures," which has just appeared, contains a description of the new Feild high-temperature viscosimeter by which the viscosity of slags can be accurately measured up to temperatures as high as

and damping the suspended system so that its motion about its axis of rotation obeys laws similar to those governing the motion of a damped D'Arsonval galvanometer. The principle is not new, but one which has been strangely neglected and not hitherto used at elevated temperatures. Unlike the familiar Stormer viscosimeter, this new apparatus is entirely free from friction, measurements being made when the suspended system is in static equilibrium. Also, the liquid under observation is not deformed at any time, but is simply subjected to a uniform shear. Deflections may be read with extreme accuracy by means of a mirror and galvanometer scale, but for many practical purposes a pointer and graduated arc are sufficiently precise.

The method is applicable to substances possessing the most varied degree of viscosity, and, on account of the difficulty which has been hitherto encountered in estimating even approximately the viscosity of very viscous substances which do not permit of a ready passage through a capillary, finds a very fortunate application in the measurement of the viscosity of such materials as asphalt, pitch, heavy oils and petroleum, varnishes, polymerized organic products, resins, emulsions, colloidal substances, glues, greases, lards, vaselines, pasty mixes, paints, lubricants, and clay slips.

A well-known plate glass company evinced an early interest in the application of the high-temperature model of the Feild viscosimeter to the measurement of the viscosity of molten glass at high temperatures, and are taking steps to make use of the method in a technical way. The method is as readily applicable to the measurement of the viscosity of glass as that of blast-furnace slags. In fact the latter require a much higher operating temperature than do most glasses, and for this reason measurements on glasses are capable of more accurate temperature control and temperature measurements.

Figure I shows the results of viscosity measurements made on a sample of a new type of asphalt, furnished by Dr. W. A. Hamor of the Mellon Institute for Industrial Research. Viscosity values are referred to the viscosity of water at 20° C. as unity. These units are therefore equal to 1/100 C. G. S. unit. The apparatus was calibrated, not against water, but against a more viscous liquid of known viscosity, e. g. castor oil, although glycerine, rape-seed oil, or liquid petrolatum might be used equally as well. The temperature-viscosity curve of this asphalt is seen to be a smooth one, with a maximum change of curvature in the neighborhood of 120° C. (248° F.).

The Bureau of Mines is taking up the matter of developing a simple yet accurate model of the Feild viscosimeter which can be most readily used in measurements of the viscosity of petroleum, heavy oils, lubricants, asphalts, etc., etc. When the design and construction are perfected, the apparatus will be given a thorough trial in the laboratories of the Bureau.

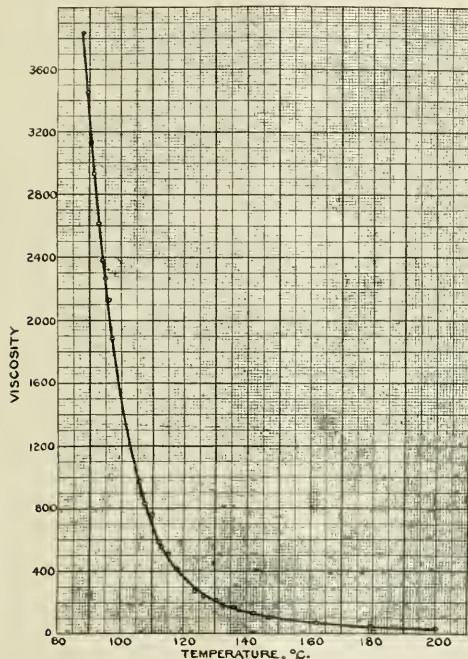


Fig. 1—Temperature—Viscosity Curve of an Asphalt Product.

1,600° C. This viscosimeter gives results which can be expressed in terms of specific viscosity, referred to that of water, or in terms of absolute C. G. S. units. A single run with the apparatus furnishes a temperature-viscosity curve over the entire temperature range desired. The principle employed depends upon the familiar law that, given two concentric cylinders—the space between being filled with the viscous liquid under examination—a torque proportional to the viscosity of the liquid is exerted upon the inner cylinder when the outer cylinder is rotated at a constant angular velocity. In the Bureau of Mines method this torque is measured accurately by suspending the inner cylinder by means of a calibrated steel or phosphor bronze suspension, and at the same time, weighting

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THE EXPANDING RELATIONS OF CHEMISTRY IN AMERICA.*

By CHARLES H. HERTY.

After a year of such strenuous service as characterized that through which we have just passed, it is well that we are again assembled for report on the work of our laboratories and for helpful conference concerning future growth and broader service. A large part of the past year's work has, through the suddenness of the call, been necessarily individualistic; the assemblage of this week furnishes the means for planning more co-ordinated effort, for mutual counsel and for deepening that spirit of co-operation which is so essential if we are to meet worthily our full responsibilities.

It is again incumbent upon me to address you. In seeking a subject I have put aside the temptation to lay before you statistics illustrative of marvelous growth during the past year, and, in spite of our belief in specialization, it has not seemed suitable to select any one line of development for tracing in thorough detail. This period is still too formative and the demands upon you too many-sided for such restricted discussion. I have, therefore, selected the broader topic "The Expanding Relations of Chemistry in America," using the present participle advisedly as indicative of growth and as mandatory of greater effort if the widening circles of chemical influence are to reach the broad shores of full-fledged accomplishment.

The dynamic center of this movement is the American Chemical Society which now consists of 8,136 members, a net growth of more than 1,000 during the year just ended. This splendid growth is not only a tribute to the energetic activities of our efficient secretary, but is an evidence of increased activity in chemistry and of a quickened realization of the need of the strongest possible national organization. The strength of this organization, however, is not measured so much by numbers as by the loyal and unselfish response of its members to every call made in its name. To this I can abundantly testify.

In considering the expanding relations of Chemistry in America let me group these under four heads—the relations to university administrations, to the national government, to our daily needs and to national thought.

I—RELATIONS TO UNIVERSITY ADMINISTRATION.

Without doubt university executives have gained during the past year a clearer conception of the fundamental value of chemistry to the nation. Aside from our own exhortations, this conception has been easy of obtainment through the increased publicity given by the daily press and by periodicals to matters chemical, through the difficulty to purchase certain needed supplies, through the feverish activity to meet these

unexpected demands, and through the call for young chemists from university laboratories. Has the conception, however been translated by the makers of university budgets into deeds which will insure an adequate response by the universities to the increased demand which is to be made upon them for chemists possessing the best possible training? I have neither purpose nor desire to criticize, nor even to attempt answer, but I do not hesitate to suggest that in these abnormal times the demands upon chemistry departments are unusually great and should be generously met if we are to view the future with equanimity. The bounds of the service of chemistry to the nation are prescribed by the character and extent of the training given in our universities. Physical equipment must be increased and bettered and staffs must be maintained adequate in number to allow full opportunity for research along with teaching duties.

The stimulus of these remarkable times upon the minds of the students is plainly evident, but here lies a danger. The expansion of existing industrial plants and the creation of new lines of endeavor in chemical industry call for many young men to serve in control work, and the call is often very alluring. It would be a great misfortune if the filling of these new positions should be at the expense of the graduate students of the future. We cannot afford an abridgment of the number of young men thoroughly trained in our universities in the methods of research. Graduate fellowships in largely increased number should be provided, for without such aid the door of opportunity will be closed to many whose full mental potentialities will be needed in the future.

The danger of losses from university ranks, however, is not confined to graduate students; already there are strong indications of a considerable raid by the industries upon the staffs of universities, and the question of professorial emolument is, therefore, not one for leisurely future consideration, but belongs to the immediate present.

To sum up, the university budget for chemistry needs prompt and decided expansion.

In the matter of co-operation between universities and industries definite progress has been made. Four important matters typify this progress.

The New York Section has conducted throughout its winter meetings a symposium on this subject, and these discussions resulted in a request of the Society that a permanent committee be appointed to carry forward vigorously such co-operation.

The General Chemical Company announced the formulation of a new policy in the creation of an advisory staff of university professors.

The Massachusetts Institute of Technology announced a Master's Course in Chemical Engineering, including a School of Chemical Engineering Practice. Through the co-operation of industrial plants a half year of systematic plant experience and training is added to the curriculum without sacrifice of thorough

*Presidential Address at New York Convention of American Chemical Society.

foundation work or training in research. In return for the privileges offered by the plants, the research facilities and the faculty of the Institute will be available for the study of special problems connected with each plant.

A joint meeting of the Puget Sound Section and the Seattle Chamber of Commerce aroused great enthusiasm and resulted immediately in the creation of industrial fellowships in the University of Washington for the study of the problems of the Northwest.

Such illustrations furnish proof that earnest thought is being given to this phase of co-operation and it is inspiring to note how quickly such thoughts are being translated into definite action.

II—RELATIONS TO THE NATIONAL GOVERNMENT.

Forty-nine members of the Society, representing the several states and Alaska, on appointment, responded to the request of the President of the United States that the chemical industries be mobilized under the program of the organization for industrial preparedness. Publication of the correspondence in connection with these appointments would furnish lasting testimony to the loyal and unselfish patriotism of the membership of our organization.

In response to the invitation of the National Academy of Science our representatives are now co-operating in the organization of the research facilities of the nation and in questions connected with the establishment of the government nitrate plant.

If we are to proceed promptly and intelligently with the development of a diversified and comprehensive chemical industry we must know the detailed character and amounts of chemical importations. The statistics now published by the government are inadequate in their itemization. The formulation of the character of the information needed is our responsibility. This is the work of the committee on Government Statistics, of which Committee Dr. B. C. Hesse is chairman. The inauguration of the work has unfortunately but necessarily been delayed. It is now well under way, and for its full consummation I beg to urge the thoughtful aid of every member of the Society, and the co-operation of each of the Local Sections. We have never undertaken any more important or fundamental work than this. If, as a result of this inventory, we are able to state in exact terms the specific character of the information needed by the chemical industries, in order to render this country independent of foreign sources of supply, we shall then have a right to expect with confidence the sympathetic co-operation of the federal authorities.

May I, under this heading, make two suggestions to the National authorities:

First.—Provision should be made in the immediate future for the storage of large quantities of government-owned toluene. With the cessation of European war orders for explosives, and with the rapid increase of by-product retort ovens for coke manufacture, we

shall eventually have a large over-production of toluene, with consequent lowering of price. The potential value of this hydrocarbon in munitions is too great to allow its sacrifice as a fuel or as an illuminant, and its storage involves no unusual difficulties. The moral effect alone of its known presence in our midst would in itself fully justify the investment as a preparedness measure.

Second.—Modern warfare is largely dependent upon the successful work of chemists, not alone in the direct production of munitions, but, through research, in husbanding the resources of the country, and in increasing knowledge which in times of stress may be vital to the nation. In view of the now well recognized fundamental character of such work the military authorities should formulate a definite policy in regard to the chemist, whereby in times of war his services may best be applied to the advantage of his country. The lack of such a policy during the recent enlistment of the National Guard has in several cases interrupted lines of research whose successful outcome would prove much more vital to the power of the army than the presence of the individuals bearing arms. England somewhat tardily recognized that her chemists were more needed at home than at the front, and, therefore, recalled them.

III—RELATIONS TO OUR DAILY NEEDS.

The economic developments of the past two years have emphasized the close relation between normal daily needs and the activity of chemists, particularly through certain shortages which have brought economic distress. Among these shortages three stand out pre-eminent—motor fuel, potash for fertilizer and coal-tar products, particularly synthetic dyestuffs. Let me discuss the first and second of these briefly and the third somewhat more at length.

Motor Fuel.—The enormous annual increase of motors using gasoline as fuel, together with the largely increased export of this material, has resulted in greatly increased price of this product. To meet the situation chemists have naturally turned their attention to the "cracking" of the residues of crude petroleum, furnishing thus some relief. In view, however, of the uncertainty of petroleum supply such efforts cannot prove the ultimate solution of the problem. With the cessation of the war further aid may be expected from the benzol recovered in the by-product coke oven plants. With this at its maximum, however, it is estimated that it would equal only 10 per cent of the motor fuel now consumed. Plainly we must look further for the permanent supply, and that seems to me to be alcohol. I am fully aware that there is nothing original in this suggestion. It is mentioned rather for the purpose of urging greater consideration of the problem by chemists, who must solve the problem, by manufacturers of motors who have such great interests at stake, and by lumbermen who, in their mill waste alone, possess the raw material from which, by processes in operation today, alcohol

could be produced equal in volume to 40 per cent of our present gasoline consumption.

What striking advance in this line could be confidently expected if the automobile manufacturers and lumbermen of the nation would join forces with chemists in the creation of a great research laboratory where the problems of motor fuel could be vigorously attacked, not by the "green powder" method of recent notoriety, but by common sense, scientific investigation, conducted by the ablest of chemists and chemical engineers, unfettered by tradition and filled with the conviction that the day of genuine new things will never end.

Potash.—To meet our present shortage of this valuable fertilizer constituent we have sought relief feverishly through the kelp fields of the Pacific coast, the alunite deposits of Utah, the feldspars, blast furnace and cement works waste, and have as yet obtained but slight relief. Something noteworthy may yet result from these earnest efforts, especially through the aid of the appropriation of \$175,000 by Congress for further investigation of kelp, but at present we seem to have adopted the general policy of waiting until the war is ended.

Let me, in this connection, remind you of the old problem: namely, the rendering available *in situ* of the potash now in the fields in the form of silicates. The records of the U. S. Bureau of Soils show that the average weight of a foot acre of the sandy soil of the cotton belt weighs 1,750 tons, and contains an average of 0.1 of 1 per cent potash, or $1\frac{3}{4}$ tons K_2O per acre, while the clay soils average in weight 2,000 tons per foot acre and show an average potash content of 1.68 per cent of 33.6 tons K_2O per acre. From this material nature slowly supplies available potash for plant food through the action of the soil solution upon the potash bearing silicates, but the process is too slow. Many lines of research are in daily progress in our laboratories whose object is the discovery of "accelerants" for certain chemical reactions. Does not the importance of this problem and its altogether normal character demand of us greater effort to find a suitable accelerant for this world wide process. The problem is easy to state; its solution has as yet proved impracticable. May we not hope that the activities of physical chemists through studies of the soil solution and its action upon the mineral constituents of the soil will be ultimately successful?

Coal-Tar Dyestuffs.—It is unnecessary for me to remind you at this time of the great disturbance of our industrial life which resulted from the cessation of imports of German dyestuffs, nor of the rapid extension of the by-product coke oven whereby we are now assured of a far more than adequate supply of raw material for an American dyestuff industry sufficient for American needs. It is a pleasure to testify to the energy and resourcefulness of our dyestuff manufacturers, who, in spite of competition with the munitions industry for coal-tar crudes and for necessary

acids, and with uncertainty as to the future constantly dogging their steps, nevertheless have notably contributed to the relief of the dyestuff famine.

It is my purpose, however, to trace, for the sake of the record, the efforts made during the past two years to obtain legislative assurance of a fair start in the upbuilding of a well rounded, permanent industry, and to point out the character of the legislation which on the last day of the present session of Congress became a law of the land. It is a distressing story, humiliating to all who wish for our country freedom in every possible form. Here is the story.

Immediately after the outbreak of the war the New York Section of this Society, foreseeing economic distress from possible shortage of dyestuffs, appointed a representative and politically non-partisan committee to report on the prerequisites of an adequate self-contained American dyestuff industry. The report, unanimously adopted by this the largest of our local sections, recommended congressional enactment of protective duties amounting to 30 per cent *ad valorem* and $7\frac{1}{2}$ cents per lb. specific on finished dyestuffs, one-half these amounts on intermediates and an effective anti-dumping clause. The protective rates of this report formed the basis of the Hill bill, introduced in the House on the opening day of Congress by Representative Ebenezer J. Hill, of Connecticut. In January, 1915, hearings were held on this bill and there was presented the unusual sight of both producers and consumers urging the Ways and Means Committee to report the bill favorably. In spite of this unanimity the report was not forthcoming. Public demand for such legislation, however, increased, and finally, after a conference between leading members of the controlling party in both the Senate and the House with representatives of a large number of producers and consumers, a form of legislation was proposed by the congressional representatives which embodied the *ad valorem* rates of the New York Section but reduced the specific duties by one-third, such specific duties to continue in full force for a period of only five years, after which time they were to decrease 20 per cent annually. Another feature was the proviso that if at the expiration of five years American dyestuff factories were not producing 60 per cent of the values (note this carefully) of American consumption, the specific duties were to be immediately and completely repealed by Presidential proclamation.

In spite of the lowered specific duties, this agreement, confirmed by authorized interviews from Washington, led to increased activity by many producers. It is not difficult to imagine, therefore, the amazed surprise which greeted the appearance of the dyestuff section of the General Revenue Bill, which, while it contained all of the above, showed one other totally unexpected feature, viz., the exclusion of indigo and alizarin and their derivatives from the benefit of the special duty of 5 cents per pound. Such an exception was fatal to the purposes of the bill. The *ad valorem*

duty alone would not suffice to promote and encourage the manufacture of synthetic indigo and alizarin. No scientific or technical justification existed for discrimination against these two coal-tar dyes, which constitute 29 per cent of the values of our consumption. Furthermore, the manufacture of at least 10 per cent of dyestuffs could not for the present be attempted in this country because of existing foreign patents. Such considerations show that the possibility of expansion of the home industry within the five-year period to 60 per cent of the values of consumption would be precluded by the terms of the bill itself. Consequently the duration of the special duty for any dyestuff would be restricted to the initial five-year period. Evidently our lawmakers had surpassed the skill of the alchemists, in that they had demonstrated their ability to transform at least bricks into gold.

Pressed for a justification of the exclusion of indigo and alizarin, the chairman of the Ways and Means Committee made explanation on the floor of the House in a speech which by previous agreement was to conclude the debate. In this speech reference was made to the satisfactory character of the conference with the representatives of the industries; individual manufacturers were referred to as not desiring full protection for indigo and alizarin; and no justification on scientific or technical grounds was attempted. Then the dyestuff section of the bill was adopted by a party vote. Immediately briefs were filed with the sub-committee on the Senate Committee on Finance in charge of this section of the House bill. These briefs included letters and telegrams from the individuals referred to in the House debate refuting the statements made by the chairman of the Ways and Means Committee. Moreover they pointed out clearly that the exception of indigo and alizarin was not in accordance with the original conference agreement and would prove disastrous to the entire industry. The Senate sub-committee was convinced and accordingly struck from the bill the objectionable exceptions, and in addition included natural indigo and coal-tar medicinals and flavors, additions in every sense logical, and giving to the classifications of the bill a thoroughly comprehensive character.

With the appearance of the printed hearings and briefs an interesting exhibit was made by the plea of a large consumer of indigo located at Greensboro, North Carolina. Not content with the discrimination given indigo in the measure as passed by the House, he urged its complete removal to the free list. No other consumer of indigo joined in this request. The sub-committee rejected his plea.

The completed section of the Revenue Bill was then endorsed by the full committee and by the majority party conference, and was adopted by the Senate. In the last hour of the session the section emerged from the joint conference of the majority party conferees from both Senate and House with indigo and alizarin excluded from the special duty, and carrying along

with them, as a sort of legislative by-product, medicinals and flavors. As no record is published of the proceedings of conference committees we are left to assumptions as to the influence which prevailed to give the section its final form; but in the light of the history of the legislation and the personnel of the conferees, as published in the Congressional Record, it is not difficult to imagine whose influence was determinative in maintaining the discriminating feature of the original House legislation, against which united protest has been made, save for the voice of one consumer. The section in this disastrous form was then adopted by both Senate and House and is now the law of the land.

Such is the answer of the present Congress to the nation-wide (with one exception) call for adequate protective duties for the encouragement and upbuilding of this much-needed industry. The claims of this industry, upon non-partisan legislative aid, are reasonable, because of initial difficulties in manufacture and the character of the competition to be met after the war. These claims are also commanding, through the intimate connection of the industry with adequate munitions for our army and navy. Nevertheless, the measure, professedly enacted for its upbuilding, stands today stamped with the evidence either of the most specialized form of legislation for special interests, or of stupidity, as a tax placed upon the consumer without the benefit of an assured home industry, or of stubbornness in maintaining a wrong position rather than admit an error in judgment. I do not believe the citizens of this nation will set the seal of their approval upon such legislation.

IV—RELATIONS TO NATIONAL THOUGHT.

In the light of the activities of the past year let us ask ourselves frankly, "What is the position of chemistry today in the thought of the nation?" No one can doubt that it occupies a much more prominent place. This is due in part to the superb response American chemists have given to the sudden call upon their resources and ingenuity, in part to the advertisement through the press of the important role of the German chemist in the industrial upbuilding of that nation, and to the constant repetition of the phrase that modern war is largely a matter of chemistry and engineering.

Concrete evidence of increased appreciation of chemistry is furnished by the Second National Exposition of Chemical Industries now in progress. Its exhibitors are more than double those of last year; its exhibits show many new products, born of the exigencies of the year; its underlying thought has been broadened to include a more systematic showing of the importance of chemistry to the wise use of natural resources; and its purposes have gained a far wider and more appreciative understanding by our people as a whole.

Again we find evidence in the recent issuance of a special chemistry edition by a prominent trade jour-

nal, The Manufacturers' Record. The purpose of that unusual issue was not merely to emphasize the advantages of a great section of the country for the up-building of chemical industries, but, of far greater importance, it sought to vitalize the thought of the people of that section as to the fundamental character of chemistry among the factors of industrial development.

Furthermore, it must be noticeable to all that slowly but surely an educational campaign is getting under way in the daily press and in periodical literature which will eventually result in the arousal of our people to a full comprehension of the value of chemistry as a national asset.

These are simply signs of the times. We cannot, however, feel that the national thought has as yet grasped in its entirety the all-pervading influence of chemistry so long as Cornell University, with its strong chemistry staff, must delay the replacement of its burned laboratory through lack of funds; so long as Johns Hopkins University, the cradle of American chemical research, must undergo such struggle for the means to erect a new laboratory on the beautiful new site of that institution; so long as members of Congress view chemists and chemical manufacturers as fit subjects for hard bargains; so long as railway presidents feel that chemistry has no part in the development of the natural resources of the sections traversed by their lines; and so long as waste in any form is allowed to continue unheeded.

Further expansion of the relations of chemistry to the national thought involves:

First.—Continued educational effort through the press. Plans for such are being evolved, and these plans are meeting the quickened sympathy of the leaders of the press. Each of us must co-operate in this work. As a class we are not qualified to write in popular style, and in the past we have not troubled ourselves very much about such matters; but we can furnish facts and sound opinions to those who have the work and responsibility of popular presentation, and we should stand ready, each in his own community, to share in such co-operative effort.

Second.—An awakening of the financial interests of the country to the fact that the ways of chemistry are not mysterious but applied common sense which constitutes a sure guide.

Third.—Continued worthiness of our efforts. This is our direct responsibility. Thoroughness of training, untiring zeal in work, aggressive conservatism in counsel, courage in new undertakings, independence in thought, generous co-operation, constant search for truth—these must surely lead us to that vantage ground where we can best serve this our country.

The value of the tar, ammonia, benzol products, naphthalene, and coke produced in the United States in 1915 was \$80,816,975.

THE USE OF BARK FOR PAPER SPECIAL-TIES.*

By OTTO KRESS.†

In the manufacture of paper from wood pulp, if the bark is not carefully removed preliminary to the pulping of wood by either chemical or mechanical processes, it appears in the pulp and produces small specks in the finished paper, detracting from the appearance and value of the sheet. Some kraft mills do not clean their wood preparatory to pulping, depending on the alkaline digestion to destroy the bark. This practice is followed only to a very limited extent as the high consumption of chemicals in the pulping of bark and unevenness in shade and uniformity of the resulting pulp are decided drawbacks. The loss in barking will depend on the nature and condition of the wood, and on the method of barking of the wood, and will vary from 10 to 25 per cent, based on the weight of the rough wood.

According to the census of 1911 of the Department of Commerce, there were consumed in the United States 4,328,052 cords of pulpwood, of which 280,534 cords were classified as slabwood and other mill waste. Practically all of this wood was cleaned and barked before pulping. The bark, as removed at the mill, is saturated with water and even with heavy pressing can be made only about 50 per cent dry, so that it is of comparatively little value as fuel. One mill that brought this matter to our attention loaded the daily waste from the drum barking of 100 cords of spruce wood into gondola cars, and disposed of it by filling in low places around the mill. They experienced difficulties from the odors of the decomposing bark, from fires which are apt to occur and which are hard to control, while the cost of removal was estimated at from \$15 to \$20 a day.

Large quantities of waste bark in the tanning industry are likewise awaiting successful utilization. Waste tan bark from the leaches is about 35 per cent dry, and has an estimated fuel value of \$0.60 in comparison with \$3.00 for bituminous coal.¹ The latest census figures from the Department of Commerce and Labor on tan bark production for 1909 showed a production in the United States of 698,365 tons of hemlock bark and 324,070 tons of oak bark, valued at \$0,968,710. The production since then, however, is reported to have diminished steadily, because of the increased use of chemical tanning agents, and accurate data as to the present amount is not available. Such minor uses for the waste bark as that in the white lead industry, runways for stables, etc., take but a very small amount of the bark, leaving the balance for fuel after the tannin extraction.

Other sources of waste bark in the United States are the lumbering of redwood, cedar, etc., where the

*Paper presented Sept. 29 at meeting of the Technical Section of the Paper and Pulp Association, New York City.

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¹J. Am. Leather Chem. Assoc., 11, 361.

bark is a decided detriment both in the lumbering operation and at the sawmill. The Forest Products Laboratory in attempting to utilize these wastes for pulp and paper purposes first attempted to reduce the bark by chemical pulping. A decided drawback is the small yield and very heavy chemical consumption. As the various waste barks such as spruce, redwood, extracted hemlock bark, etc., all have different properties, it was next attempted to reduce them to a pulp condition by simple mechanical reduction in the beater and Jordan and after mixing with various longer fibred pulps, to run them over our experimental machine into various paper products. The apparatus used in these experiments at the laboratory was a 40-lb. beater, a small Jordan, and a 15-in. experimental Pusey and Jones Fourdrinier machine.

A paper was made at the laboratory on the basis of 80 per cent extracted hemlock bark and 20 per cent kraft pulp which showed such remarkable impregnation towards tars, asphalt, etc., that it appeared advisable to make further tests on a mixture of hemlock bark and rag stock to try and cheapen the felts used for roofing and shingle stock. A co-operative study was undertaken with a company manufacturing roofing felts to work this out on a commercial scale. Samples made at the laboratory on a basis of 60 per cent rag stock and 40 per cent waste hemlock bark, showed a good strength and good saturation. A factory trial was then arranged for and roofing felt was made on a 114-in. trim cylinder machine. The beaters in this trial were loaded very heavily, using 9,800 lbs. of 33 per cent dry bark in the ordinary 1,200-lb. beater. The bark was beaten for one-half hour with the roll down to reduce the larger pieces, and then dropped into a separate chest from which it was pumped to a Jordan and dropped into the machine stuff chest. Felt ends were used for convenience instead of rags. They were opened up in the beater, dropped into a separate beater chest, brushed lightly in a separate Jordan, and then mixed with the ground bark in the machine stuff chest. The percentages of rag and bark were controlled by regulating the amount put through the separate rag and bark Jordan, the discharges from which were mixed in the machine stuff chest. The mill in which this trial was made ordinarily makes chip and box board, and to avoid unnecessary dirtying of the machine, only the two end vats of the possible five were used. Various runs estimated up to 80 per cent bark and 20 per cent felts were made, and no difficulty was experienced in passing the paper over the machine or in drying. Using two vats, only thin felts could be made of an average calibre of 40 to 45 points. The backwater, while reddish in color from the soluble coloring matter removed from the bark, was comparatively free from fiber. In this trial 6,000 lbs. of finished felts were made, and the rolls were later impregnated and finished into roofing at two different plants.

Felt made on the basis of 80 per cent bark would of course be too weak to stand up under the weakening action of the hot asphalt and would break under the tension of pulling the felt through the saturating tank. Felt carrying this high percentage of bark was made at this trial in order to bring out to the maximum extent the difficulties that might be expected in the mill production.

A co-operative study was then undertaken by the laboratory with the saturating plant, a felt mill and a tannery to develop the practical use of tan bark in the manufacture of roofing felts. At the present time, the co-operators are using at certain mills having an average daily production of 50 tons of felt, approximately 60 tons of dry bark a week, which is shipped, 40 per cent dry, from the tannery. It is reported by the co-operators that roofing felt is being successfully made and offering no undue difficulties in the saturating plant on a furnish in which tan bark is used up to 20 to 30 per cent. The average price of rags for the manufacture of felts at the present time is \$40 a ton, and conversion loss is estimated to average 25 per cent. The value of waste bark for fuel as already stated is \$0.60 per wet ton, 35 per cent dry, in comparison with bituminous coal at \$3 per ton. To this must be added the cost of handling the bark into the cars, the profit to the tannery, the expense of plant facilities necessary in changing the tanner's fuel to coal and in rearranging side tracks and loading facilities, and the freight rate to the felt mill. If this freight rate is high, it would appear to be advisable to consider the cost of drying the spent bark from a 66 per cent moisture content to about a 15 per cent content, and thus avoid the freight on the water. Modern drying apparatus has made possible the cheap drying of raw materials to a remarkable degree. This drying might offer difficulties in obtaining the necessary minimum car weight, as the spent bark is bulky.

One of the difficulties still to be overcome which, however, we feel can be easily solved, is the controlling of the percentages of bark and rag stock run onto the felt machine. At first the bark, after passing through the bark Jordan, was mixed with the beaten rags in the beater rag stuff chest, then pumped through the rag Jordan to the machine chest. This offered considerable difficulty, as any variations in pumping, in the level of the stock in the chests, etc., caused a variation in the percentage of bark in the finished felt. In order to hold the percentage of bark constant the Jordaned bark may be pumped to a separate chest with overflows arranged at 10, 20, 30 per cent, etc. The bark can then be run by gravity to the various rag beaters or the right amount can be run directly into the rag stuff chest in proportion to the amount of rags dropped. Where this development work has been done, the felt is now made on a 72-in. felt machine with a 36-in. cylinder and 46 3-ft. dryers. It has been found by experience that no beater treatment for the bark is required. The bark at the present

time is screened through a screen with about a $\frac{3}{4}$ -in. mesh, and is thrown into the chest. From here it is pumped to the regulating box on the Jordan and the discharge from the Jordan run to the beater rag chest. The mixture of rags and bark after passing through the rag Jordan goes to the machine chest and then onto the machine. The object of the screening of the raw bark is to prevent the choking of the inlet pipe to the Jordan by the larger pieces of bark. The larger pieces which are screened out are thrown into the beater with the rags and reduced to a proper condition in this way. A valve placed on the discharge pipe from the Jordan was found to be a convenient way to regulate the fineness of the stock, as it enables the operator to regulate the time of Jordaning. This direct Jordaning of the bark makes a decided power saving in the beating, for if a considerable replacement of rags is made by the bark, less beaters are required for the same felt output.

No difficulty is experienced in either forming or running the sheet. A little difficulty has been experienced in the proper drying of the felt, when a large percentage of bark is used. In order not to curtail the production by slowing down the machine it would appear advisable, if the mill is so arranged as to permit it, to add some extra driers or arrange for some special drying device. Due to the higher specific gravity of the bark, the finished felts are a trifle heavier, and allowance must be made for this in running the stock. The felt mills today are receiving a poor grade of rags, in fact only such rags as can hardly be used for any other purpose. With a more careful selection of the rags, we believe that it will be possible to raise the percentage of bark in the finished felt and still maintain the quality of the finished goods. Further, it is possible that the Jordan is not the best machine to reduce the tan bark to a proper condition; probably a special refining engine will reduce the bark without unduly cutting the fiber found in the bark. The limitation to the use of a higher percentage of bark does not appear to be in the paper mill, but in the lack of strength in the saturating tanks; this is partly due to the moral inertia and prejudice of the men handling the felt through the saturating tanks. A great deal could no doubt be done by using a better grade of rags that could be readily paid for by only a slight increase in the percentage of bark in the finished felt, as there is such a great difference in the cost of rags and bark.

Two other rather interesting and possible uses for waste hemlock and oak bark have been worked on at the laboratory. Two papers were made at the laboratory on the basis of 80 per cent extracted hemlock and 80 per cent extracted oak bark, the balance in each case being unbleached sulphite pulp. These papers were unsized and had a tendency to dust off fine particles of bark on rubbing, which we believe could be overcome by sizing. Two of the rolls were printed on a commercial 12-color wall paper printing machine,

the paper taking the colors well. One of the disadvantages of a grade of paper of this type is that the high specific gravity of the bark makes the paper heavy. Hanging is ordinarily made on a furnish of 80 to 85 per cent ground wood, the balance of sulphite, and a decided saving would be made, if a wall paper made on a basis of 80 per cent bark could find application. The paper made with hemlock bark had a decided reddish color, while the oak bark paper was more of a chocolate shade. We have tried out in a preliminary way the color effect of cheap mordants, such as iron sulphate, etc., and find that there is a possibility of changing the shade with very little expense. The present price of this grade of paper was estimated by the wall paper printing concern at \$60 to \$80 a ton. The paper printed better than the ordinary oatmeal wall paper with which it is compared, and if no undue difficulties are experienced in running it on large and fast commercial machines, it should be decidedly cheaper than the present hanging. This paper would undoubtedly have the disadvantage of increased weight and possibly the disadvantage of dusting off small particles of the bark.

Two rolls of unsized paper were made at the laboratory on the basis of 80 per cent extracted hemlock bark and 80 per cent extracted oak bark, the balance sulphite, and tried out on a commercial machine for making fiber conduits. The paper was run at the mill in competition with their ordinary grade of paper, and impregnated thoroughly; it made a satisfactory conduit which could be machined and which showed up well under the various tests applied. The paper in which bark was used was thinner than the regular grade, and further, was softer, and impregnated more readily, which might require a slight change in the blending of the saturant. A decided drawback lies in the fact that the increased weight of the bark makes the conduit decidedly heavier, thus increasing the freight rate on the finished conduit.

Trials were made at the laboratory on the possible utilization of spruce and balsam bark obtained in the drum barking of pulpwood. These barks differ from waste tan bark in being pitchy, which would exclude their use in any product which subsequently had to be impregnated. Further, any large percentage of spruce bark makes a brittle sheet. For certain purposes such as wall board, where the finished board is usually made by plying together the individual sheets by a binder such as sodium silicate, this tendency towards brittleness is of little consequence. A co-operative study was undertaken with a wall board mill but the work to date has not progressed beyond the laboratory stage. Boards made experimentally on the basis of 80 per cent waste bark, the balance sulphite and kraft, also boards on the basis of 50 per cent bark and 50 per cent ground-wood, were favorably commented on by the mill.

Spruce bark offers some difficulty in mechanical reduction and we believe that the beater will require

extra sharp tackle, and a special filling in the Jordan would be a decided help. At the laboratory no difficulty was experienced in reducing spruce bark in 45 minutes in an experimental beater, while on a commercial beater, fitted with dull tackle, a 5-hour treatment still left the bark in an unsatisfactory condition.

Patent specifications on the uses of waste bark for pulp and paper purposes have been submitted to Washington by Mr. Howard F. Weiss, of this laboratory, and myself. If patents for the United States are granted, they will be dedicated to the public. Foreign patents have also been applied for.

There are a great many other possible uses of the various barks which at the present time have either a limited or no value. A fair insulating board has been prepared at the laboratory from the bark of the redwood tree. Other possible uses that suggest themselves are the use of spruce or balsam bark from the drum barking of pulpwood which is to be mixed with sulphite screenings and run into car liners. Further, waste hemlock and oak bark might be used in the manufacture of sheathing, carpet liners, bottle wrappers, deadening felts, chip board and box board. A small percentage might be used for board used in stand up boxes where no great bending qualities or high test are required. For indurated fiber ware, such as pails, etc., it might be possible to substitute a large percentage of ground tan bark for the more expensive stock used at present.

The above remarks can be looked upon as only indications of what might be done, as each mill will have to determine whether they can substitute bark in part for a more inexpensive stock, and still maintain the quality and standard of their product. Waste bark can be looked on only as a filler, and must be used with a longer fibered stock to carry it over the machine. Its use will permit a decided saving in many grades of paper products.

The Third National Chemical Exposition.

That the Third National Exposition of Chemical Industries will be a great success is already assured. An additional third floor has already been engaged, and plans are being made to use the fourth floor. In addition it is hoped to have large sections showing the resources of the country awaiting development.

Two prizes have been offered to the students of Cooper Union Art Schools to draw up a poster seal for the next exposition. The designs for this purpose will be finished January 1st next year, and prizes awarded February 1st. All designs submitted and which the jury consider fit, will be exhibited during the next exposition.

The value of the total mineral output of southeastern Alaska for 1915 exceeded \$6,000,000, and included: Gold, \$5,400,000; copper, \$300,000; silver, marble, lead, and gypsum, \$300,000. Most of the gold came from lodes in the vicinity of Juneau.

A LABORATORY FLOTATION MACHINE.*

The first flotation work done in the Missouri School of Mines laboratory was with a standard slide machine described in Hoover's book on flotation. This machine gave good results but difficulty was experienced with grit getting in the lower bearing of the

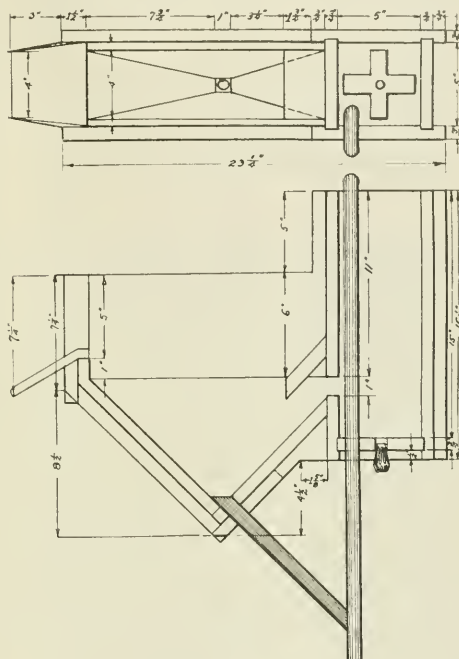


Fig. 1.

impellor shaft causing it to wear excessively and to leak.

A Mineral Separation type machine after the model described in the Engineering and Mining Journal, Sept. 4, 1915, was then built in the laboratory. The first modification made was to add 2 in. to the height of the agitator box to lessen the loss due to splashing, to put another agitator to the impellor and to add a glass plate in each side of the spitzkasten for the purpose of judging the nature of the froth.

The next change was to add an air lift to increase the circulation of the pulp. The spitzkasten was next made longer to give the particles of gangue held mechanically in the froth a better chance to settle. This required a larger charge to fill the machine. The width of the spitzkasten was made smaller to reduce the size of the charge. This has an operating volume of 9,000 cc.

In order to keep down the charge required and at the same time get the advantages due to the long spitzkasten, the volume of the spitzkasten was reduced

*From Bulletin of the School of Mines and Metallurgy, University of Missouri.

by shaping it as shown in the machine in Fig. 1. The air lift was connected to the center of the bottom of the spitzkasten, thereby lessening the amount of accumulation on the bottom of the machine. This machine was used by McCartney in his oil tests. This machine has an operating volume of 3,600 cc. and was built in the School of Mines laboratory at the following costs:

Wood	\$ 2.50
Labor	5.00
Impellor shaft-material and labor	1.25
Pulley for three speeds	.50
Tinwork	1.50
Bearings, 2½ in. "Dodge" brass split bearings ..	5.00
Grease cups, 2 No. 000 tiger	.50
Motor, ¼ H. P. Western Electric, 1,700 r.p.m.	
at 200 volts D. C.	25.85
Belting, ¼ in. round leather at \$2.83 100 ft.	.17
	\$42.27

The Sulphuric Acid Industry Prosperous in 1915.

The production of sulphuric acid in the United States in 1915 was 3,868,152 short tons, expressed in terms of 50° acid, valued at \$29,869,080, and there was an output of 189,795 short tons of oleum or fuming acid of different strengths, valued at \$2,787,971, making a total of 4,057,947 short tons, valued at \$32,657,051. These figures, which are made public by the United States Geological Survey, and which were compiled by W. C. Phalen, include so-called by-product acid, or acid produced at copper and zinc smelters. The production of acid from this source in 1915 was 1,056,830 short tons, expressed in terms of 50° acid, valued at \$7,042,126, and included also 59,189 short tons of oleum of different strengths, valued at \$579,115. The total production is an increase as compared with 1914, due to an increase in the production of acid of the stronger grades—60° and higher. The output of by-product acid in 1915 also showed an increase as compared with 1914. Expressed in value of products these increases have been large. In preceding years the Survey has reduced the different strengths of acid, including the stronger grades, to 50° Baumé whenever sufficient data were available for this conversion. The manufacture of this stronger acid is becoming more important, owing to the demand from the explosives and war munitions industries, and in the statistics for 1915, for the first time, this acid is classified separately. The price of sulphuric acid varied widely during 1915. Producers who had previously entered into long-time contracts sold acid at prices much below those now current, especially during the last part of the year. The trade in strong acids was active, on account of the demand from the explosives and war munitions industries, but this demand came only after the first quarter of the year and was very strong only during the last half of the year. Before that time some acid plants were shut down. Average values are therefore much below those which ruled on the market at the close of the year.

TOTAL SULPHATES IN LEATHER.*

By DR. L. E. LEVI and AUG. C. ORTHMANN.

In a former article we mentioned the fact that we had some 2,000 odd leather analyses to make during the year. It is but natural that the most rapid and accurate methods be used in order to clear the way for other work.

We have found it highly essential to make the total sulphate determination in all leathers finished or unfinished, that have been tanned with a chrome sulphate compound. This determination in conjunction with the chromium content will readily show the absence or presence of free sulphuric acid in the leather.

Where a basic chrome sulphate liquor has been used for tanning and the basicity further reduced by subsequent addition of alkali carbonates or hydrates after the leather has been chrome tanned, to further set the chrome, and after thorough washing with water, free sulphuric cannot be present. The sulphuric acid found in such a case would be combined with chromium, aluminum, iron, calcium, sodium and potassium, the last two are entirely removed on proper washing, thus by determining the chromium and the sulphates, and calculating the latter to H_2SO_4 , the proportion of one to the other will determine the chrome compound present, due allowance must be made for acid combined with aluminum, iron and calcium.

Normal chromium sulphate ($Cr_2(SO_4)_3$) is a combination of 38.78 per cent Cr_2O_3 and 61.22 per cent SO_3 and if this proportion exceeds these figures it is a sure sign that free acid is present.

Realizing the importance of this determination in that the basicity of leather could be easily controlled, the matter of selecting a rapid and accurate method for the same suggested itself. The bomb method, the nitric acid method and the method of Balland and Maljean have been used in this laboratory up to the year 1914. These methods, however accurate, were found wanting regarding rapidity, neither of which could in any way be improved upon in this respect. The bomb method; an Emerson calorimeter bomb was used for this purpose, 1 gram of leather was placed in a platinum shell which in turn was placed in the bomb, the lower part of the bomb was covered with sodium carbonate, then filled with oxygen at a pressure of about 25 atmospheres and ignited by means of an electric current and iron wire, the released gases were led into a beaker containing N/10 alkali and the solid contents of the bomb were washed into this beaker with hot water, the whole acidified, boiled and filtered, the filtrate boiled and treated with $BaCl_2$.

The nitric acid method of Wuensch and the sodium carbonate method of Balland and Maljean were carried out as given in Procter's Leather Industries Laboratory book, 2nd edition, pp. 370 and 371.

*From the Journal American Leather Chemists Association.

The method we finally adopted, is as accurate as any of the above and at the same time more rapid than any of them. Chromic acid strongly acidified with hydrochloric acid is used to oxidize the organic matter and any chromic acid not reduced in this way is reduced by means of alcohol, the remaining alcohol and resulting aldehyde are boiled off. The method is carried out as follows:

The Reagent.—Take 50 grams of chemically pure potassium bichromate and dissolve in 150 cc. of water; when dissolved add 50 cc. of chemically pure concentrated hydrochloric acid. Weigh out in 1 gram of the fat free leather into a 250 cc. beaker and add 20 cc. of the reagent and bring to a gentle boil, then add 8 to 10 cc. of hydrochloric acid, let digest over burner until all organic matter is destroyed. Then boil vigorously for 2 or 3 minutes after which add about 50 cc. water and about 5 cc. of alcohol, boil until all chrome is reduced and alcohol and aldehyde is driven off, then add 50 cc. more water, bring to a boil and add barium chloride solution, let stand 2 or 3 hours, filter and wash precipitate and burn as usual.

In case a leather contains talc or allied substance filtration must take place before adding barium chloride.

A comparison of the different methods follows. One gram of finely divided fat free leather was used.

	Weight BaSO ₄ grams.	Calculated to per cent H ₂ SO ₄ .
Bomb method	0.1032	4.3375
	0.1020	4.2870
Wuensch's nitric acid method...	0.1034	4.3459
	0.1017	4.2744
Ballard and Maljean sodium carbonate method	0.1024	4.3039
	0.1032	4.3375
Chromic acid method	0.1012	4.2534
	0.1015	4.2660

In articles published by the authors (this *Journal*, July, 1914, and September, 1915), we had the pleasure of giving to the leather chemists methods as used in our laboratory with the hope that all other members of our association would give our members the benefit of their knowledge and experience of the various methods used by them in their laboratories so as to bring us one step nearer to the realization of that goal to which we are all striving, namely, the standardization of methods. We are very sorry to say that our hopes have been almost blasted. We say almost blasted because we think the bright light of the aurora of uniform methods will penetrate the dark recesses of inactivity and awaken our fellow chemists to give for the benefit of all their most valuable experiences and thereby brighten the field of uniformity.

The annual statement on the production of gold, silver, and copper in Alaska in 1915 is now available for distribution by the United States Geological Survey, Department of the Interior. The value of the total mineral output of Alaska during the year is stated as \$32,854,229, as compared with \$19,065,666 for 1914.

OBSERVATIONS UPON THE ATMOSPHERIC CORROSION OF COMMERCIAL SHEET IRON.*

By E. A. RICHARDSON and L. T. RICHARDSON.

The corrosion of iron and steel is a question that is becoming of increasingly great importance. The problem of finding the true nature of and the ultimate causes that underlie the rusting of iron is as yet unsolved. Much work has been done in the past, is being done at present and before the problem is solved, much more will undoubtedly be done in the future.

The paper will not burden itself with a lengthy review of previous work that has been done upon the subject, but will confine itself to a brief summary of such work.

As regards the relative merits of wrought iron and steel much work has been done, but observations on the two materials seem to be in poor agreement.

Of recent years the question of the rust-resisting properties of copper-bearing steels has arisen and remains as yet unsettled, the chief contenders being the makers of copper-bearing steel and those of pure iron. As far as numerical data are concerned, the advocates of copper-bearing steel seem to be in the lead, in fact it seems to the writers that one weakness in the argument of the pure iron advocates is that they give little numerical data to support their claims. To many, their arguments would carry much more weight if such data were included.

Briefly, up to about 1910, a considerable amount of work had been done upon the subject of copper in steel, but this work was mainly in the form of fragmentary observations on steels that contained small quantities of copper either accidentally or intentionally added, and a few actual tests upon copper-bearing material. Previous to this time there appeared to be no acute controversy as to the effect of copper in steel upon corrosion, although judging from the literature it did exist at this time to a rather mild extent as to the effect of this metal upon the physical properties of steel. The general impression, one would gain from reading these articles, is that copper in steel is a benefit as regards resistance to corrosion.

Shortly after 1910 copper-bearing steel was put upon the market as a corrosion-resisting material. The controversy then became acute, the chief objectors being the advocates of pure iron. The result has been that a considerable amount of work has been done and published without settling the question. Most of this work seems to have been done by those inter-

*Paper presented at the 30th General Meeting of the American Electrochemical Society, in New York City, Sept. 28-30, 1916.

¹Buck, D. M. *Copper in Steel*—The Influence on Corrosion. *Jour. of Ind. and Eng. Chem.*, June, 1915.

²Buck, D. M., and Handy, J. O. Research on the Corrosion Resistance of Copper Steel. *Jour. Ind. and Eng. Chem.*, March, 1916.

³Friend, J. N. The Corrosion of Iron and Steel, p. 251.

⁴Sang, A. The Corrosion of Iron and Steel, p. 81.

⁵Aston, James, and Burgess, C. F. The Rate of Rusting of Iron and Steel. Eighth Int. Congress of Applied Chem., 26, 453.

ested in copper-bearing steel in their efforts to prove that this material is the real rust-resisting material they claim it to be. A large share of the published work, which contains results from tests closely approaching actual service conditions, has been done by Mr. D. M. Buck²—a strong advocate of copper-bearing steel. The opposing side appears mostly in discussion of these and other papers and appears to be taking a defensive stand. The impression, gained by the writers, from reading the available published evidence, is that copper-bearing steels do possess rust-resisting properties and are superior to any iron or steel now on the market.

Likewise, the influence of mill-scale upon the corrosion of iron is under discussion.

Friend³ for instance states that "traces of oxides upon the surface of metals are powerful stimulators of corrosion."

A. Sang³ says, "Black oxide only protects provided it is continuous and firmly anchored to the iron (Bower-Barffing, etc.); as mill-scale, which is loose and fissured, it is detrimental, the iron in contact with it and exposed rusts about 50 per cent faster."

Aston and Burgess¹ find "that mill-scale had an accelerating effect for an atmospheric test and a retarding action for a fume test." Further they state that "there is no doubt that the protective property of mill-scale is dependent upon its physical properties, continuity, etc."

G. C. Whipple and M. C. Whipple⁵ tested steel, ingot iron and wrought iron with mill-scale and with mill-scale removed and obtained erratic results, but, generally speaking, the rusting was slightly greater in the case of the metals from which the mill-scale had been removed than in the cases of the metals on which the mill-scale had been left. They state, however, "that the best remedy to protect steel from pitting is to remove mill-scale."

Buck and Handy² in their latest paper state "at the time of exposure of the full-sized corrugated sheets careful notes were taken concerning the physical appearance of the sheets as affected by the amount of mill-scale which was present, and as to whether they were outside or inside in the pack. During the progress of the test this feature was carefully watched, and the time of ultimate failure of sheets whose surfaces were comparatively free from mill-scale was compared with others of the same grade, whose surfaces were well covered with mill-scale. From these observations, we concluded that the influence of this original surface oxide is slight, and is lost in the early stages of rusting, for no difference in final failure could be noticed."

One thing, however, in regard to many tests that have been made upon the relative corrosion of iron

and steel, is that insofar as the ultimate consumer is concerned, they are not of the greatest value, since many times only two or three materials were compared, or the materials were made especially for test and cannot be obtained in commercial quantities. Such tests do not carry the most weight since they do not have the air of disinterestedness that exists in the case of materials purchased upon the open market. In fact one of the arguments of the pure iron advocates is the objection to "special tests" and the demand of basing comparisons upon service tests only.

In view of the fact that no results had been published of a complete test on commercial materials, it was deemed desirable to make a test containing all the types of iron and steel that could be obtained.

Some of the kinds of materials that are commonly used for structures, exposed to atmospheric corrosion, are:

1. Steel.
2. Puddled pure iron.
3. Commercially pure iron.
4. Copper-bearing steel.
5. Cast iron.

This paper deals with the first four classes.

Accordingly there were obtained upon the open market the following materials in the form of black sheets of 26 gauge:

1. Bessemer steel.
2. Open Hearth steel.
3. Charcoal iron.
4. Commercially pure iron.
5. Commercially pure iron.
6. Copper-bearing iron.
7. Copper-bearing steel.
8. Copper-bearing Bessemer steel.
9. Copper-bearing Open-Hearth steel.

These materials analyzed as follows:

	Copper.	Manganese.	Carbon.	Phosphorus.	Sulphur.	Silicon.
1	Trace	0.300	0.01	0.087	0.054	
2	Trace	0.413	0.01	0.079	0.041	
3	0.044	0.031	0.01	0.050	0.024	0.020
4	0.016	0.028	0.01	0.009	0.025	
5	0.028	0.009	0.01	0.006	0.024	
6	0.237	0.006	0.01	0.004	0.054	
7	0.181	0.100	0.01	0.003	0.027	
8	0.256	0.315	0.08	0.092	0.046	
9	0.268	0.387	0.01	0.052	0.024	

Before starting a work of this character, which involved quite some labor, due consideration was given to the methods of testing and in particular to those methods about which there is some difference of opinion. Questions arose concerning the desirability of a previous heat treatment and the necessity and means of removing mill-scale previous to testing.

Opinions differ as to whether samples of iron should be tested just as received or whether all test-pieces should receive some treatment so that the physical properties will be as nearly identical as possible. One author contends that samples should be tested as purchased, since the material that the samples represent will be used just as purchased. On the other

¹Whipple, O. C. and Whipple, M. C. Mill-Scale as a Cause of Corrosion. Eighth Int. Congress of Applied Chem.

²Buck, D. M., and Handy, J. O. Research on the Corrosion Resistance of Copper Steel. Jour. Ind. and Eng. Chem., March, 1916.

hand, there are those who contend that all samples tested should have as nearly the same treatment as possible. They suggest, therefore, that the test-pieces be annealed at the same temperature and that mill-scale be removed.

It would seem that the method used for testing should depend upon the results to which the data is to be put. If the results are intended for the ultimate consumer the material should be tested just as purchased since this is the condition that it is used by the ultimate consumer. On the other hand, if the data is for scientific purposes such as determining the effects of various elements in the material, all variables other than the ones under investigation should be removed if it is possible to do so.

However, to make the work as broad and as complete as possible, it was decided not to limit the test to one method, but to try out both ways and to determine the relationship between the two.

Since part of the specimens were to have the mill scale removed, the question arose as to what method should be used for removing this scale. In previous published work, very little has been said about the method of cleaning test specimens. When stated, however, it has usually been done by mechanical means such as filing or grinding, or by chemical means such as acids. Experiments were, therefore, conducted on the effects of methods of removing mill-scale upon the subsequent corrosion. The results of these experiments have already been published.⁷ It was shown in this paper that methods of cleaning by the use of chemicals had a profound effect upon the rate of corrosion, especially on tests of short duration.

In the contemplated test a clean iron surface was necessary in which the surface iron was in the same physical and chemical state as the iron beneath the surface. It was, therefore, decided that removal of the mill-scale by pickling in sulphuric acid, thorough washing with water and drying and subsequent removal of the surface iron with fine emery cloth would give a surface that was identical with the material itself.

The question also arose as to the method by which corrosion was to be estimated. There is a choice of methods to determine the rate of corrosion. One method commonly used is to determine the loss in weight after exposure for a given length of time and considering this loss as an index of corrosion. Another method is to allow the test specimens to corrode until failure occurs and to take the length of time as an index of corrosion. Inasmuch as there is some question as to the reliability of the "loss in weight" method, it was thought best to continue the test to the failure of the specimens.

This made it necessary to decide upon some standard condition at which failure could be considered to have taken place. Evidently, failure should not be taken at a point when the iron has completely rusted

away or even when it has almost disintegrated, since any sheet iron in service would be of no value long before such a condition obtained. The point of failure selected was when the sheet iron was in such a condition that it could be seen to be perforated when the rust was removed by gentle tapping with a blunt object such as a file or nail. By using one specimen of each kind of material as a test piece that was tapped and examined at intervals of about two weeks, a close approximation to the time of failure could be obtained. Thus the other specimens were not molested until the latter part of their useful life and the effects of tapping were practically eliminated from the results. By this method, it is believed that the life of each material was obtained to within an error of three or four weeks. The sheets of 26-gauge iron were accordingly prepared for test by cutting into pieces 5 in. by 8 in. (12.7 cm. by 20.3 cm.). For the test on the material as received ten pieces of each kind of iron, that were found by measurement to be of standard thickness, were used. For the test on the prepared material, a number of pieces of each material were annealed at a red heat and then cleaned by the method already described. Great care was taken to give all of these test pieces exactly the same treatment. Ten of the prepared specimens of each material that were found by measurement to be of the same thickness were taken for test. These prepared pieces were of practically the same thickness as the "as received" samples tested, due, no doubt, to the extreme thinness of the mill-scale.

On account of the precautions taken as regards uniform thickness of materials, the method of estimating failure and the method of cleaning surface, it is believed that the test should be comparative.

All samples were then placed securely in a wooden rack and exposed to the weather May 24, 1914. The atmosphere was what might be described as a semi-country one, and cannot be taken as at atmospheric acid test.

At the very start a marked difference was noted in the character of the rust formed on different materials. Whereas, on the Bessemer and open-hearth steel samples, the rust was of a yellowish-red color and became loose rapidly, the rust on the others was dark red in color and much more adherent. This adherent state seemed to reach its maximum in the copper steels, where the rust was very dark and fine grained.

The life of the different materials tested is given below; each figure being an average of ten test pieces and represents the time for failure in days:

	Material as Received.	Material Annealed and Surface Cleaned.
1	348	363
2	357	381
3	615	558
4	598	437
5	675	467
6	743	601
7		
8	1,200 (estimated)	1,200 (estimated)
9		

⁷Richardson, E. A. The Effect of Pickling on the Corrosion of Iron. Met. and Chem. Eng., 12, 759.

From visual observations at this time there appeared to be little difference between pure irons with or without additions of copper.

At the present writing the three samples of copper-bearing steel are still in good condition. The rust is still adherent and the underlying metal is still intact. The life of these steels have been estimated at 1,200 days, which figure the writers believe is very conservative. These specimens are still exposed to the weather and will be until failure occurs.

Conclusions.—Taken as a whole, the results indicate that copper-bearing steels are, without doubt, decidedly superior to any of the other materials tested. The remaining materials may be divided roughly into two classes, one class including the ordinary steels (Bessemer and open-hearth) and the other class, the commercially pure irons and the copper-bearing irons. Charcoal iron is classed with the pure irons. We have obtained results in another test which would indicate that the resistance of wrought iron to corrosion is due to the purity of its iron and not to slag inclusions. In addition, it was noted during the present test that charcoal iron appeared to corrode in very much the same way as pure iron.

In regard to the steel-iron question it is noted that the pure irons (including charcoal iron) are superior to steel. It is believed that this superiority is due to the purity of the iron, or to some combined effect of manganese and copper.

The results obtained in regard to the effects of mill-scale do not agree with the results obtained by others. They indicate that with steels which rust rapidly, mill-scale is a stimulator of corrosion. On the other materials tested, the mill-scale has exerted a protective action. We have no explanation for this.

The important feature of the results, however, is that it substantiates the claim made in several other publications that the addition of copper to steel in amounts of about 0.25 per cent causes a remarkable increase in its ability to resist atmospheric corrosion. In the present test, the addition of about 0.25 per cent copper to Bessemer or open-hearth steel has resulted in an increased resistance of 300 or 400 per cent.

The addition of copper to pure iron also results in an increased resistance to corrosion, but to no such an extent as the addition of a similar amount to steel. The addition of about 0.25 per cent copper to a commercially pure iron results in the useful life being increased by about 20 per cent. This figure was arrived at by comparing the average life of irons Nos. 3, 4 and 5 with No. 6.

We have been unable to determine the reason for this effect of copper in reducing corrosion. It is believed, in view of the fact that the copper exerts a greater influence in steel than in iron, that it must be due to the combined presence of copper and manganese, since the chief difference in the iron and steels under consideration is in the manganese content. It may be that the copper eliminates a harmful effect of

manganese, or it may be that it is some combined effect of these two elements that acts as a protection to iron. The writers are inclined to believe that it is the latter cause.

This conclusion, the writers believe, is also confirmed by the results of other observers. Mr. D. M. Buck* tested several kinds of sheet irons and steel by exposing pieces 2 in. by 4 in. (5.08 cm. by 10.16 cm.), 27 gauge, to the atmosphere in a mill yard at McKeesport, Pa., and found the loss in weight after eleven months to be as follows:

No.	C.	Mn.	S.	P.	Si.	Cu.	Loss*	Condition of Test-Pieces After Exposure.
E	.01	.30	.043	.065		.31	2.65	No holes.
V	.01	.39	.078	.111		.31	2.75	No holes.
Z	.04	.43	.049	.099	.011	.25	2.83	No holes.
D	.06	.50	.037	.046		.26	2.94	No holes.
C	.06	.33	.035	.018		.25	2.96	No holes.
H	.042	.16	.024	.003		.21	3.05	Few holes in 2 pieces.
O	.027	.07	.033	.007		.09	3.31	Few holes in 4 pieces.
W	.049	.05	.043	.005		.10	3.72	Many holes in all pieces.
J	.022	.03	.031	.006		.034	4.17	Many holes in all pieces.
I	.03	.06	.013	.052	.039	.07	4.26	Many holes in all pieces.
Y	.04	.45	.046	.099	.006	Trace	6.94	Only a lace work of steel left.

*Loss given in oz. per sq. ft.

Similar results were obtained upon tests made at Scottdale, Pa., and in McKeesport city water. These tests indicate that copper even up to 0.10 per cent added to low manganese materials increases their resistance to corrosion but little. Ordinary steels containing about 0.40 per cent manganese, but no copper, are very poor as regards resistance to corrosion but additions of copper to such steels result in a greatly increased resistance. A maximum resistance is reached with about 0.25 per cent copper. These results were also confirmed upon full-sized sheets of the same materials and in the above cited papers several excellent photographs are given.

The writers believe, in view of these results, that the resistance of pure iron to corrosion could be increased by the addition of both manganese and copper and that additions of manganese to pure iron or steel, even up to 3 or 4 per cent, or more, with a corresponding increase in copper to produce a maximum effect should give a material more resistant to atmospheric corrosion than the copper steel now on the market.

Also, some interesting results might be obtained by substituting for manganese in copper-bearing steels or irons, chromium, vanadium, tungsten, or molybdenum.

SUMMARY.

1. Copper-bearing steels are decidedly superior to pure iron, steel, or charcoal iron.
2. The addition of copper to pure iron increases its resistance to corrosion, but to no such an extent as similar additions to steel.
3. Charcoal iron and pure iron are superior to

*Buck, D. M. Recent Progress in Corrosion Resistance. Amer. Iron and Steel Inst., May, 1915.
Also pamphlet, Keystone Copper-Bearing Steel. American Sheet and Tin Plate Co.

steel as regards resistance to atmospheric corrosion.

4. Charcoal iron is very similar to pure iron in its resistance to corrosion.

5. Copper is believed to decrease corrosion due to some mutual influence of manganese and copper.

6. The additions of large amounts of manganese and copper to pure iron or steel are suggested as well as additions of copper-chromium, copper-vanadium, copper-tungsten, or copper-molybdenum.

7. Mill-scale stimulates corrosion in rapidly rusting materials and retards it in slowly rusting materials.

Spelter Production in 1916.

The following figures are not final and may be revised a small fraction of one per cent. The regular mid-year statement will be issued by the United States Geological Survey, Department of the Interior, some time this month:

SPELTER STATISTICS, JANUARY 1-JUNE 30, 1916.

Supply:	Short tons.
Stocks on hand January 1.....	14,253
Production from domestic ores.....	267,449
Production from foreign ores.....	48,756
Imports	464
	330,922
Withdrawn:	
Foreign exports	20,197
Domestic exports	58,007
Stocks June 30.....	24,000
	102,204
Apparent consumption, approximately.....	228,700
Number retorts, June 30, 1916.....	193,696
New retorts building or contemplated.....	22,188
	215,884

German Substitutes for Copper.

The Iron Age states that war substitutes for the 6 per cent by weight of copper, which on the average goes into the manufacture of a German locomotive, are reported to be in part as follows: The fire-boxes and stays, previously of copper, are now made of cast iron. All the smoke and steam tubes and the oiling cocks and thin pipes are of weldless drawn steel. For the rod-bracings, axles, grease-boxes and the bracing parts, the difficulty is believed to have been overcome by using cast iron and a special alloy called flange metal which is a mixture of tin, lead and antimony. It is regarded as possibly dangerous to use this metal unless the pins and axle journals were previously bushed with white metal. Cast iron was used for piston-boxes, side valve rods, frames and lubricators, lubricator covers and step bearings. Bronze covered with vulcanized rubber, which was the standard metal for the various handwheels, is being replaced by cast-iron wheels covered with ordinary string or jute fabric. German engineers are now experimenting with a new rolling process for preparing the flange metal referred to, having an equivalent of bronze which will dispense with antimony. A question is raised as to the life of such engines.

THE COMMERCIAL FERTILIZER INDUSTRY IN THE UNITED STATES.*

By LESTER W. TUCKER.†

Reliable statistics regarding the fertilizer industry in the United States are very hard to obtain. The Census of 1910 places the fertilizer industry forty-eighth in rank in the value of products of manufacture, and gives the number of establishments engaged in the manufacture, the number of persons employed and the capital invested as follows:

Number of establishments	550
Total number of persons employed.....	21,950
Capital invested	\$121,537,451

The tonnage of fertilizer used in the various states is given in a report issued by the Department of Agriculture of the United States in 1898, and also in a special bulletin from the same source for a part of the states from 1906 to 1909 and for all of the states from 1910 to 1913 inclusive. The fact that the close of the fiscal year in various states is at different periods causes a wide variation of yearly results in trying to correlate these figures. However, the figures give a fairly good idea of the amount of fertilizer used in each of these various states for the years given.

The growth of the industry in value of product since 1860 is shown by the United States Census for 1910 to have been as follows:

Year.	Value of production.
1860	\$ 891,344
1870	5,815,118
1880	23,630,795
1890	39,180,844
1900	44,657,385
1905	56,541,253
1910	103,960,213

The increase in value of product from 1905 to 1910 is much greater in proportion than it has been for the previous years shown. This increase has been caused to a great extent not only by the greatly increased use of fertilizer for the cotton crops in the South and for many of the northern states, but also by increase in value of products. The increase in consumption from 1905 to 1911 is largely due to the increased use of fertilizer in the so-called cotton belt and adjoining states. The annual rate of increase has been nearly the same in both the cotton belt states and the states north of them, if we neglect the normal increase of the years 1910 and 1911 in the cotton belt states. This annual increase appears to be, under normal conditions, about 200,000 tons per year in both groups of states.

The number of plants engaged in the industry in the various states is very indefinite. The United States Census in 1910 gives the total number of plants as 550 for the entire United States, while the State of Georgia Year Book for 1913 gives a list of persons and factories engaged in the industry as 415 in that

*From the September Journal of the Boston Society of Civil Engineers.

†Managing Engineer, Westinghouse, Church, Kerr & Co., New York.

one state alone. Eliminating from this list the cotton seed oil plants and the persons who are simply acting as selling agents for certain mixtures, the total number of plants is reduced to about 135, which, if we take into account the factories recently built, agrees closely with the United States Census Reports for 1910. The figures in the year books of the various states include so many selling agents and cotton seed oil plants that they are not reliable indices of the actual number of manufacturing establishments. From a careful perusal of the number of establishments given in the 1910 Census, and from a personal knowledge of many of the factories in the eastern part of the United States, the writer believes that the figures given in the United States Census for 1910 are practically correct and has adopted them in this paper. This number for the last twenty years is as follows:

Year.	Number of establishments.
1890	390
1900	422
1905	399
1910	550

Grouping the various states in order to study the growth of the industry since the first available statistics were taken in various sections of the United States shows that the greatest consumption has always been in the cotton states. The New England states show a substantial increase, especially in Maine, while the Central states show large gains in the last ten years. The states west of the Mississippi River show a very small consumption, it being very evident that the soil in that section has not yet been exhausted to the extent where commercial fertilizer is necessary. In Texas, one of the greatest cotton-producing states in the South, there is a comparatively small use of fertilizer, which from the 1912 and 1913 reports would not seem to be increasing to any great extent. California shows a small increase, which it is expected will continue in the future, as the use of fertilizer in the fruit and vegetable crops is found beneficial.

The annual increase in the United States for the past six years has been an average of about 480,000 tons per year, the maximum increase being from 1909 to 1911, when the increase was 900,000 tons per year. The increase in the future, while subject to the same business conditions as all other industries, must, as a whole, continue to show a substantial growth if the agricultural interests are to be maintained at the same rate of progress in the future as in the past.

The manufacture and use of what is officially known as commercial fertilizer in the United States dates back to about the year 1840, when a commodity known as Peruvian guano was brought into the United States from the islands off the west coast of South America. Some years later, in the early sixties, the manufacture of a fertilizer made from fish and sold under the name of fish guano was begun, and several other mixtures under various names were also put on the market about this time. The discovery of potash salts in Germany and the teachings of Dr. Von Leibig

were followed by the discovery of phosphate rock in South Carolina in 1867. Acid phosphate was then first introduced as a part of these fertilizers, and it is with the manufacture of this kind of commercial fertilizer that this paper will deal directly.

The enormous use of commercial fertilizer in recent years has been possible only through the discovery of the phosphate rock in the United States and the potash salts of Germany, the supply of Peruvian and other guanos being practically exhausted, and the fish products are nearly all used in conjunction with the phosphate. It is the phosphate rock and potash

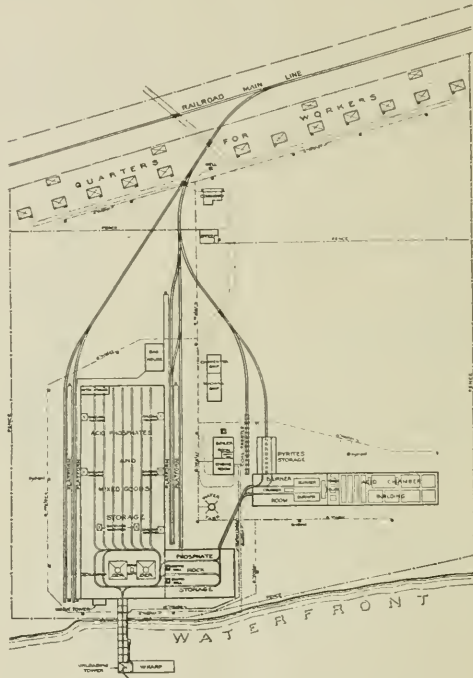


Fig. 1—Typical Layout for Fertilizer Factory.

which today make the manufacture of commercial fertilizer an important industry.

The manufacture of commercial fertilizer is practically the same wherever it is carried on. Factories are located all the way from Maine to the Gulf and from the Atlantic to west of the Mississippi River. Several cities have become important centers for the manufacture of fertilizer, being chosen by the various companies on account of their superior locations for receiving and forwarding material as well as for distribution centers.

Phosphate rock is shipped from the mines in as nearly a dry condition as is possible and is received at the various factories and kept in this same dry condition until it is ready for the grinding or pulverizing.

A complete fertilizer establishment consists, in a general way, of a factory building with its attendant

storage sheds, acid plant, bag factory, power plant, office, shops and general quarters for the employees, together with facilities for receiving raw material and shipping out the finished goods. Many of the factories do not have an acid plant connected with them, buying their acid in bulk as needed.

A typical cross section for a factory is shown by Fig. 1 to give an idea of how the rock is handled from the time it leaves the ship or car in which it is received from the mine until it is finally deposited in the shape of acid phosphate or base goods in the storage sheds.

A description of an acid plant is not necessarily a part of this paper, but it can be said that such a plant consists of a furnace room in which are located the furnaces for burning the sulphur or pyrites, the towers for denitration of the gases and acid, and chambers for the condensation of the gases to acid.

Raymond, Kent or Sturtevant mills, which pulverize it until it passes through the No. 100 mesh screen which is a part of the mill. From these mills the pulverized rock passes by means of screw conveyors and elevators to the storage bin over the mixing floor. Also over the mixing floor is located an acid tank for the storage of sulphuric acid. Immediately below the ground-rock bin is located a weigh hopper for weighing the rock used, and a small measuring tank for measuring the acid used. Immediately below the mixing floor, and on a level with it, is the mixer. Mixers are of various makes, but are similar in operation. They consist of round iron cylinders about 18 in. deep and 8 ft. in diameter in which are installed paddles or stirrers working in opposite directions. These mixing pans are located directly over large receptacles called dens into which the mixed materials are

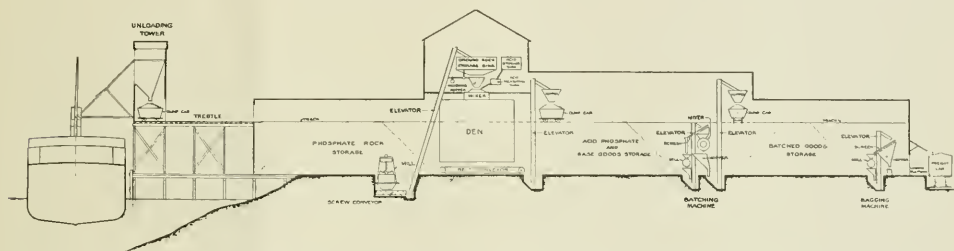


Fig. 2—Diagrammatic Cross Section of Fertilizer Factory.

Roughly speaking, a ton of acid is required for each ton of phosphate rock used. The acid most commonly used is sulphuric acid (H_2SO_4) at a density of 50 degrees, Ba. scale.

The fertilizer factory consists, for the major part, of storage space. Most of the factories are obliged to furnish storage for the equivalent of nearly their entire year's output. For example, a factory may have an output of 60,000 tons, and storage space must be supplied for acid phosphate and base goods for practically this total amount, as the shipping season for nearly all the factories lasts only about six weeks and there must be on hand, at the beginning of the shipping season, acid phosphate, base goods and mixed goods for practically the total output of the factory. A factory can be said roughly to consist of storage for phosphate rock, mixing floor and machinery, dens, conveyors, tankage, batching and bagging machines, and storage for acid phosphate, base and mixed goods. The typical cross section of a factory shows in a very general way how the materials are handled from the time they are received at the factory until they are shipped out in the finished state.

The phosphate rock, upon being received at the factory, is taken from the vessel or car and placed in the storage pile. The first process which it goes through is that of grinding, or pulverizing, the rock being taken from the storage pile and put through a Griffin mill or some of the later types of mills used especially for phosphate rock, such as the Bradley,

dumped. The method of operation is to dump into the pan the proper amount of ground rock from the weigh hopper, following it immediately with the proper amount of acid, which is carefully measured. The pan is then started and run the necessary length of time to mix the contents thoroughly, which are then dumped into the den. This procedure continues until the den is filled.

In the manufacture of base goods, the proper proportion of ammoniates is added to the contents of the mixing pan with the acid and phosphate rock so that the whole mass may become thoroughly mixed before going to the dens. The dens are made airtight, except for a flue leading to the wash tower in which is located a fan carrying off the fumes arising from the chemical changes which take place. These fumes are condensed in the wash tower by means of sprays in order to prevent the obnoxious odors from being generally spread through the atmosphere. Many of the factories have gone to a great deal of expense in building wash towers so that the fumes shall cause as little trouble as possible to the surrounding country, and there are many plants where, a few hundred feet away, it would scarcely be known that any such operation was being conducted.

It will be noticed that careful weighing and measuring of all stock used is one of the most noticeable things about one of these factories.

The mass remains in the den for about twelve hours, after which time it has become thoroughly cooked, and

is then removed to piles in the storage buildings until it is ready to go to the batching machines. A batching machine consists of a boot for the deposit of the various ingredients which are to be batched, elevators, shaking screens, mixing machine and pulverizers. From the boot the ingredients are elevated and passed over screen to eliminate all hard lumps, the material which passes through the screens being passed through the mixing machine and then taken by an elevator and carried to a hopper on the top floor. The lumps or balls which are rejected by the screen are passed through a cage mill or pulverizer, where they are broken up and again passed through the boot and mixer before going again over the screens. In the batching machines the various potash, nitrate and other ingredients to make up the proper mix are added. The batched material is then stored until ready for bagging. It is then taken from the storage piles, passed through the bagging machines, which are somewhat like a batching machine, but without the mixer, where it is again pulverized, the lumps being taken out and only the fine material going into the bags. The bags are so arranged that they are filled immediately from the spouts, automatically weighed, the bags sewed and placed in the car for shipment. In some factories the batching and bagging machines are combined, but the continuity of the operation is somewhat interfered with when this is done. A batching machine will batch from 40 to 50 tons per hour, while a bagging machine with two spouts usually bags from 20 to 25 tons per hour. In the shipping season these bagging machines are running practically twenty-four hours a day, for, as before stated, the entire tonnage of one of these factories has to be turned out in the very short shipping season which precedes the planting time in the various communities. Goods are seldom batched until they have been from seven to ten days out of the dens, as the tendency to lump is very much greater if batched sooner than this. Fertilizer will not set after being milled a second time, and it is for this reason that the batched goods are put through the pulverizer a second time.

There are so many different grades of commercial fertilizer on the market that it would be impossible to give any description of the various formulas by which they are manufactured. All of the fertilizers in which phosphate rock is used are based on three principal ingredients—acid phosphate, ammoniates and potash—and it is the number of parts of each one of these three ingredients which give to the fertilizers as sold their various names. In practically all the states of the Union it is now necessary to stamp on the bag the formula under which the fertilizer is manufactured. In several of the states each bag has to have a state tag attached, certifying as to the formula under which it is mixed, the number of pounds in the bag, and the exact parts of each ingredient going in to make the mix. In New Jersey, Georgia, South Carolina, Alabama and some other states, the sale of

these tags by the state practically fixes the amount of fertilizer sold within the state. In other states the formula and weight must be printed in letters at least $\frac{3}{4}$ in. high on the outside of the bag. In nearly all of the states the requirements are such that inspectors from the various agricultural bureaus have the right to make an analysis of the contents of any single bag, and if it is found to be at variance with that shown on the tag or the printed formula on the bag, the manufacturer is subject to heavy fines. For interstate traffic the United States Department of Agriculture has various inspectors who go into any factory and take samples of the mixed goods for analysis to see that they are as stated in the formulas. In fact, it is safe to say that the contents of a bag of fertilizer are as near what the formula on the bag states as it is possible to make it, and this applies wherever it is sold in the United States.

For one who is not actively engaged in the manufacture of this product and who passes through a factory on a casual visit and sees the number of men rushing about with wheelbarrows, one with potash, one with nitrates, another with additional ammoniates, it is impossible to realize that at every machine where these various loads are dumped, everything has been carefully weighed and every particle of the ingredients going into a single batch will check out in the end with the formula which is printed on the bag. To get these various mixes right and to keep them right in their various handlings through the factory with the class of help which is here employed, would seem to be almost impossible, and that it is done and that the formulas are very seldom found to be wrong when the fertilizer is inspected shows the thoroughness of the organizations by which the various factories are managed.

An industry connected with all of the plants where any large amount of fertilizer is manufactured is the making and printing of the bags in which the finished product is shipped. The jute from which the bags are made comes in large rolls and the bags are cut, sewed and the name and formula printed on them in the bag factory. This part of the industry is hardly to be classed as coming under the general head of this paper, but it is an absolute necessity and of considerable importance, and at many plants which have been visited great care and ingenuity have been shown in the ways and means of making and printing these bags.

The power plants connected with the various factories vary in size and equipment according to the necessities of the plant. As a general thing, it can be said that these are up to date and entirely adequate to the necessities. Of course many of the older plants have machinery which is rather out of date, but it is of such efficiency that will not warrant changing it. The power required varies so much at the different seasons in the year, being a maximum during the shipping season of only six or eight weeks and a minimum

practically the rest of the time, that a plant is not justified in installing new equipment for this short season when the old will carry them through and is perfectly adequate for ten months in the year. All the modern plants are electrically driven, having individual motors for all machines, so that the use of power for all parts of the factory is limited to the requirements of each machine.

One of the necessary parts of the power equipment is the pumping plant, which has to be of a capacity sufficient not only to supply the wants of the factory, but also to keep the fire protection system under pressure at all times.

At all of the plants where goods are manufactured, a laboratory is maintained and chemists are engaged the year around in testing the goods, checking formulas and in experimenting on changes in existing formulas. As practically all formulas used have to be registered in the various states where goods are sold, this department is one of the most important and one in which the greatest efficiency has to be maintained.

The writer has visited nearly one hundred fertilizer plants located in all parts of the United States. In the factories of the northern states the lower classes of white labor are generally used, while in the southern states negro labor is employed exclusively. In the southern part of California, the Mexican peon is employed, while in the vicinity of San Francisco, Chinamen of the lower class are used. In all cases the labor may be said to be of about the lowest class, and when it is considered that with this class of labor, superintendents and foremen in these various factories ship thousands of tons of fertilizer, mixed in some cases to as many as forty different formulas from one factory, and that these mixtures are made with practically no mistakes, it must be noted that the efficiency of the foremen and superintendents is equal to or better than that of those employed in what are usually classed as high-grade factories.

It was observed in visiting many of these plants that the superintendents and higher class foremen were not only of the better grade of Americans, but were in many cases college-bred men, quick, sharp and aggressive, working during the rush season twelve or fifteen hours a day, and making good in an industry which would not seem to be attractive as many others which they might have chosen, but which from its very exacting requirements keeps them in a high state of efficiency and up to a stiff standard of responsibility all the time.

The condition of both buildings and equipment of the plants which have been visited can be said to have been maintained equal to that which has prevailed in many other industries which the writer has visited in the last several years. The large number of new plants which have been started since 1910 is especially noteworthy, and while there has been a slight setback for the last year or so, due to delayed sales resulting

from the present war and lack of potash from Germany, it can be said that few industries present a better outlook for future growth. In conclusion, it can be said that with the great increase in the use of commercial fertilizer in the United States which will be necessary to maintain the output of the soil and which will result from broader education in the use and economic value of fertilizer, the engineer, be he civil, mechanical, electrical or chemical, will be called upon more and more to work out the general ways and means and the detail of the various parts of this industry from the mining of the rock to the delivery of the finished product to the consumer.

Pulp and Paper Prices in Norway.

According to a recent issue of the Tidsskrift for Papirindustri, Norwegian pulp prices continue to soar and the United Kingdom pays fancy prices for the odd lots available of this year's production. Bleached sulphite is quoted at \$186.67 per long ton, easy bleach at \$160 to \$173.33, strong at \$146.67 to \$160, and kraft soda at \$133.33, net cash to makers, f. o. b. Norwegian ports. In Sweden prices keep about \$67 lower. The United States continues to keep back from the market, but Sweden claims to be receiving sufficient orders from Germany.

Dry mechanical pulp is firm and scarce at \$40 to \$41.33 f. o. b. per ton, while that which is 50 per cent moist has advanced. The current value today is \$14.67 to \$17.33 per ton, f. o. b. Norway. The demand is good, but the stocks are small. Baltic mechanical pulp mills seem to be working at full pressure, as it is understood that 40,000 tons for prompt delivery have been taken up by the German market at about \$8 f. o. b. per ton.

For the first time in several months the paper market is not rising. There is now actually a stagnation in prices, and the market on the whole is a little easier. There may be several reasons for this, but it is believed that it is partly due to the fact that France does not pay the prices lately demanded. The French newspapers have formed a buying syndicate, and it is said, too, that Scandinavian prices are again considerably higher than those demanded by Canadians. A few varieties other than newsprint, such as grease proofs, are also a little easier, whereas better-class papers are almost unobtainable. Mills making paper for the Chinese market are in an awkward position on account of the shortage of tonnage. Large lots of paper booked for March and April shipment have not been forwarded by the steamship lines, owing to lack of room; thus the stocks of the mills are large. Relief, however, is in sight.

According to La Cronica Mercantil, of Valparaiso, new fields of calcium borate are said to have been found near Iquique, and that 150 claims, or 18,750 acres, have been solicited. Average values of 15, 20, 30, 40 and 60 per cent of borax are given.

PHYSICAL AND CHEMICAL PROPERTIES OF COTTON.

A paper of considerable interest to the chemist was presented at the recent convention of the National Association of Cotton Manufacturers, at New London, Conn., Sept. 14-16, by Prof. William Harrison of the University of Ledd. The paper described experiments on the investigation and physical and chemical properties of cotton, and was, in part, as follows:

Under the microscope cotton fibres present the appearance of a flat, ribbon-like band, more or less twisted on its longitudinal axis. The fibres possess a central canal, but the ends farthest away from the seed are closed. When examined in polarized light between crossed nicols the fibres show strong illumination, Figure 1. This is due to the presence of strains in the material composing the fibre. This fact was established by the observations that (a) the effect can be produced in cellulose films by artificially produced strains, Figure 11, and (b) that the removal of the strains by the action of a solvent on the fibre removes the property of showing illumination between crossed nicols, Figures 7 and 8. In Figure 7 illumination only persists in portions of the fibres which remain under strain where the "rings" of the barrel-shaped formations prevent complete swelling.

The amount of illumination shown by cotton fibres is polarized light between crossed nicols, depends on the position of the fibres with respect to the plane of polarization of the incident rays. The maximum illumination is shown when the fibre is at 45 degrees to the plane of polarization, and the minimum when parallel or at right angles to this plane. From similar experiments made with stretched strands of india rubber it has been concluded that the fibre must be either under longitudinal tension or compression. There is no optical method of distinguishing between these two conditions, but the fact that ordinary cotton fibres behave in a similar manner towards strong caustic soda, to fibres which have been fixed while under tension during mercerization, is taken as proving that ordinary cotton fibres are also under tension.

This tension could be produced in nature, if the fibres were formed from a soft or gelatinous material, which gradually dried during the process of growth and subsequent ripening. There is reason to suppose that fibres are formed in nature in this manner. The irregular markings shown in Figures 1 and 2 are probably due to shrinking in the outer layers after the first solidification, and the twists in the fibres themselves due to unequal drying.

The ultra-microscopic examination of cotton fibres by means of Cotton and Mouton's prism or Zeiss cardioid condenser, gives an idea of their internal structure. By careful manipulation it is possible to avoid reflection of light from the edges of the fibres, but in order to avoid this easily, fibres were soaked

in oil of approximately the same refractive index as the material of the fibres.

Mercerization increases the fineness of structure, probably by swelling the solid cellulose portions into the spaces, yet forming still finer spaces in the swelled portions. Experiments, to be described later, are entirely in favor of this view. As already mentioned, the structure of Egyptian cotton is finer than that of American cotton, but the author has reason to suppose that the American cotton could be modified in structure to approach that of the Egyptian by suitable modifications in the method of cultivation, which would probably result from colloid-chemical investigation of the soil and of the fibres in various stages of growth.

The spiral fibres are nothing more than markings or irregularities in the structure, turned into spiral form by the twisting of the fibre either during growth or ripening or in the Schweitzer's reagent itself. The annular bands are not necessarily different from the remainder of the fibre. They may arise after the fibres are placed in the reagent, since it is known that a long cylinder of liquid or gelatinous matter is unstable and tends to form into spheres. On the other hand, they may be nodal parts pointing to periodic growth of the fibres.

The properties of those portions other than the main bulk of the fibre are readily accounted for on the assumption that they are composed of the same material, cellulose, as the rest of the fibre, but in a more compact condition, that is, in a different physical or colloidal condition. Mercerizing swells the whole material until the fibres consist of almost physically homogeneous cellulose.

To show that the direct colors are coagulated during the dyeing process the dye was mixed with a solution of gelatine, which, being a protective colloid, prevents or reduces coagulation, especially with negatively charged substances. The quality of color fixed was much reduced, the effect being greater the more salts present in the solution.

Now one of the greatest problems in dyeing is to get a "resist" towards direct colors. From the explanations above given it is apparent that to obtain such a resist the fibre must have a negative charge of such magnitude that all the positive ions present in the bath cannot reduce it below the value which repels the dye particles or ions, and prevents them arriving at the fibre. The best resists known at present are acetyl cellulose, nitro-cellulose and tannate of tin, all having powerful negative charges. The results obtained should be better when few or no salts are present in the dye-bath, or when the solutions are dilute.

The results in this paper show that the electrical theory finds considerable application in explaining the problems of dyeing, including those not explained by other theories. There are four points which must be considered: (a) The charge on the dye particles, (b) the charge on the fibre, (c) the size of the particles

of dye, and (d) the surface of the fibre, including that within its pores. There are many other problems which can be explained by this theory, but they require further knowledge of the last two factors, and will be left for future investigation.

In considering either the fixation of a dye by a fibre or the removal of it, the effect of the various conditions, reagents, etc., on all the above four points must be taken into account, and since these factors may be altered differently many complicated effects can be foreseen.

It was found that when cotton was exposed to light in air that in addition to the so-called oxycellulose, substances soluble in water were formed, which were of an acid character and possessed strong reducing properties. On account of the small quantity of these substances formed it was not possible to determine what the acids were. It was shown, however, that the formation of these substances had an important bearing on the fastness to light of direct cotton colors.

An idea of the nature of the change produced in cotton by mercerization can be obtained from reactions, particularly those with iodine. In order to make clear how these reactions may be used as a means of investigation, reference will be made to some experiments on starch carried out by the author some time ago (*Kolloid Zeits.*, Vol. IX, p. 5, 1911). As is well known, when starch is boiled with dilute acids two changes occur, resulting in the formation of dextrines and starch-celluloses. It was shown that the reactions of these substances corresponded to those of starch in different degrees of dispersion.

As is well known, the swelling of cotton fibres by caustic soda is accompanied by shrinking and untwisting, but no explanation seems to have been offered for this. From investigations made, the author has arrived at the conclusion that the shrinkage is due to strains within the fibre which become active when the fibre is softened by the soda.

The untwisting of fibres on mercerization is most probably due to the strains being distributed partially in spiral form. The photographs of cotton mercerized under tension, Figures 5, 6, and 10, show the appearance expected for a material stretched while elastic and fixed in that condition, the strains being regular, both longitudinally and transversely.

The examination of fibres in polarized light affords a means of distinguishing between mercerized and unmercerized cotton. The corrugated strain lines, distinct in unmercerized cotton, are diffused in cotton mercerized without tension and entirely missing in cotton mercerized under tension. The difference in appearance of polarization also serves for distinguishing them. The difference in the appearance of the transverse sections is very considerable; the regular figures shown in Figure 10 are quite characteristic of mercerized fibres.

The action of acids on cotton is of importance on account of the fact that it often causes the tendering

of cotton goods. The substance produced by the action of acids on cotton is generally termed hydrocellulose, but the exact nature of it has not been definitely established. The most important practical point, however, is to be able to distinguish hydrocellulose from oxycellulose, the product caused by the action of oxidizing agents on cotton. The work to be described was carried out for this purpose.

It was shown by C. Koechlin in 1888 that sulphuric acid solution, 93° Tw., imparted to cellulose an affinity for basic color (Methylene Blue) after 6 hours' treatment at 15° C., the maximum effect being shown after 48 hours. At 80° C. a solution containing 100 grms. per litre (14° Tw.) was shown to produce this effect in five minutes, the maximum being obtained in 30 minutes.

SUMMARY.

It has been shown that:

1. Cotton fibres are composed of cellulose which is not physically homogenous but having an extremely fine structure.
2. Raw cotton fibres are under strain represented by a tension.
3. Cotton fibres contain cellulose in several different colloidal states.
4. The electrical properties of cotton run quite parallel with its power of absorbing mordants, direct cotton colors and basic colors, and with the fastness of shades dyed with these colors.
5. The action of light on cotton is to produce substances of a reducing nature which account for much of the fading of certain coloring matters when dyed on it and exposed to sunlight.
6. There is an organic hydroxide, tetramethylammonium hydroxide, which has a shrinking action on cotton comparable with that of caustic soda.
7. The compounds formed by the action of caustic soda on cotton are most probably absorption compounds.
8. Mercerized cotton is composed of cellulose in a different colloidal state from that present in ordinary cotton and has a higher degree of dispersion, that is, a higher specific surface.
9. The shrinking and untwisting of cotton fibres during mercerization are due to strains within the fibres, which are allowed to act when the cellulose is softened by caustic soda.
10. The lustre of mercerized cotton fibres is mainly due to the fact that they have smooth surfaces, in comparison with fibres unmercerized and mercerized without tension.
11. The section of all fibres has an important influence on the lustre, particularly if such fibres have smooth surfaces.
12. Hydrocelluloses are most probably absorption compounds of cellulose and reducing substances of a sugar-like nature.
13. The cellulose portions of these compounds may have several colloidal states, according to the acid

used and the method of treatment. With hydrochloric acid the cellulose is usually peptized, while with sulphuric acid the cellulose is peptized.

14. Oxycelluloses are most probably absorption compounds of cellulose with reducing substances of an acid character. The cellulose portions are usually peptized and for this oxycellulose is very difficult to distinguish from hydrocellulose prepared by the action of sulphuric acid on cotton.

WASTE TANBARK NOW USED TO MAKE ROOFING.

A method for using waste hemlock tanbark to partially replace expensive rag stock in the manufacture of felt roofing has been developed at the Forest Products Laboratory and is now being used commercially by co-operating mills, according to an announcement made by the Forest Service. It is stated that, in these mills, from 20 to 30 per cent of the rags is being replaced by waste bark and that the quality of the finished product is equal to that manufactured solely from rags. Members of the Forest Service who have been conducting the experiments say that the utilization of the bark will make it possible to effect a considerable saving in the manufacture of felt roofing.

According to the census of 1909, over 60,000 tons of hemlock bark were produced each year in the United States. After the tannin is extracted this bark is used for fuel purposes, for which it is said to have a value of 60 cents per ton.

The extent of the savings rendered possible by the new methods is pointed out by the fact that the roofing mills of the United States have a total estimated annual production of 237,000 tons of finished roofing of all kinds, equal to about 11,300,000 "squares." By a "square" of roofing is meant 100 square feet. The utilization of the waste bark in this industry should, it is said, enable the mills to reduce their manufacturing costs appreciably.

In addition to the use of the bark for roofing, papers made at the Forest Products Laboratory on the basis of 80 per cent of waste tanbark, have been successfully printed on a commercial twelve-color wall-paper printing machine, and give promise of being entirely satisfactory. Other paper of the same make-up has been made into fiber conduits by a commercial manufacturer.

Other possible uses of waste bark which suggest themselves, say the Forest Service paper experts, are the use of bark mixed with ground wood for the production of wall board, or with sulphite screenings in the manufacture of car liners. Studies already made at the Forest Products Laboratory indicate that it may be possible to use waste hemlock and oak tanbark in making sheathing paper, carpet liners, bottle wrappers, deadening felt, and the like.

FACTORY CONTROL IN THE MANUFACTURE OF CORNSTARCH AND CORN SYRUP.*

By A. P. BRYANT.†

The number of industries in which a certain amount of chemical control is exercised is constantly increasing, and in those industries which have a more or less elaborate system the nature of this varies with the nature of the manufacturing process and even in the same line there will be considerable variation in its extent and details.

I have been asked to tell you in a few words something about the chemical control in the manufacture of cornstarch and corn syrup, an industry which annually uses over 50,000,000 bushels of shelled corn and produces from it a large variety of products, of which starch and corn syrup are the chief. The object to be obtained in an industry of this sort is the recovery of as much of the starch of the corn as possible and the utilization of the remainder of the grain to the best advantage and with the least possible loss.

The different steps in the process of obtaining the starch separated from the rest of the corn are all mechanical, but the completeness of separation is controlled only by analyses of the materials at different stages, the results of which analyses serve as a guide for factory operations. In fact it may be said that these operations are based almost entirely upon the data furnished by the laboratory. It follows, therefore, that it is necessary to have not only accurate and representative samples, but also quick and accurate methods of analysis.

In different factories the details and extent of control will vary somewhat, but the general character is the same. In what follows I shall attempt to describe very briefly the methods more particularly as practiced in one factory.

The chemical work will naturally fall under four divisions: (1) Examination of supplies and raw products. (2) Control of factory operations. (3) Examination and standardization of finished products. (4) Special and research work.

EXAMINATION OF SUPPLIES AND RAW PRODUCTS.

The extent to which supplies are analyzed and their quality or strength thus controlled will depend upon the extent of laboratory equipment and force; the analyses may be more or less complete and will follow to a considerable extent similar control in other industries. There will be analyses of coal, lubricating oils, and general manufacturing supplies, which in this case include sulphur, soda ash, bone-black, muriatic acid, etc.; and finally the examination of the corn, i. e., the raw product. Each car of corn is carefully sampled and the moisture determined. Also, from time to time, complete analyses are made of

*From The Journal of Industrial and Engineering Chemistry.
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average samples of corn to determine the amount of protein, oil, starch, water, soluble matter, fiber, and ash present. Upon these determinations are based the comparison of the yields actually obtained with what should have been obtained, as well as the variation in treatment which may be required for most satisfactory operation.

CONTROL OF FACTORY OPERATIONS.

The manufacture of cornstarch and corn syrup may be divided into three parts: the soaking of the corn; the separation of the different parts of the corn kernel (germ and oil, hull, gluten, and starch) and the manufacture of the finished products from these.

The control in the soaking or steeping process consists in the regulation of the strength of the steep water, *i. e.*, the very weak sulphurous acid obtained by burning sulphur in a draft of air and dissolving the sulphur dioxide in a large quantity of water. The amount of sulphur dioxide is determined at frequent intervals and the relative amount of sulphur burned and water used regulated according to these tests. Later in the process further tests are made to assure the total elimination of the sulphur dioxide in the finished products. This sulphur water is used to keep the corn sweet during the period of between one and two days, while it is soaking in warm water preliminary to the subsequent operations. These involve first the tearing apart of the soft, soaked corn; then the floating of the germ on a mixture of starch and water and its removal from the rest of the corn; next the grinding of the remaining portion of the corn and the separation of the bran or hull from the starch and gluten by means of silk covered shakers or reels; and finally the settling of the starch from the gluten on starch tables.

These successive steps are all in the wet and are governed by the gravity of the mixture of starch, gluten and water, and controlled by frequent observation. The completeness of each separation is determined by the analyses of samples, either taken automatically and continuously or at frequent intervals by a sample carrier.

As an example of the way the laboratory results are used a few illustrations may be given. The completeness of the separation of the germ from the rest of the corn is determined by taking a measured amount of germ-free corn and adding it to a mixture of salt and water heavy enough to float any germ which might not have been removed in the factory process. The presence of floating germ indicates that the starch and water was not sufficiently heavy in the factory operations and the gravity is then increased. On the other hand the presence of germ which will not float because it is weighted down with starch and hull indicates that the degerminating mills are not working properly and should be attended to.

Again, a sample of the bran from the shakers or reels is tested for its starch content. This indicates

the satisfactory or unsatisfactory operation as a whole. A duplicate sample thoroughly washed over silk bolting-cloth and then tested for starch shows whether any improvement that ought to be obtained should be sought for at the mills by closer grinding, or at the shaker and reels by more thorough washing, or both.

The satisfactory separation of the starch and gluten is tested by determining the protein in the starch on the one hand and the starch left in the gluten on the other. Some light immature starch granules will of necessity be carried away in suspension with the gluten, but this must be reduced to the lowest possible amount.

The starch, which is obtained as the final result of the operations already alluded to, is used for the preparation of the various kinds of starch (such as pearl, lump, powdered, laundry, etc.), for roasting to produce dextrin, or is sent to the refinery to be made into corn syrup, or corn sugar. The gluten and bran are united, filter-pressed and made into gluten feed. The germ is sent to the oil house, whence, after due time, it emerges as corn oil and corn oil cake or corn oil cake meal.

The control work thus far outlined has to do simply with the completeness of the mechanical operations involved in the separation of the different component parts of the corn. In the refinery on the other hand a chemical change is involved in the hydrolysis of the starch under pressure and in the presence of a trace of hydrochloric acid. In the manufacture of corn syrup the hydrolysis is carried only to a point where from 40 to 50 per cent of the starch has been actually hydrolyzed, the remainder being split up into dextrins. There are found both dextrose and maltose in the hydrolyzed products, but for control work it is sufficient to determine the reducing value of the product and report this as dextrose.

The acidified starch milk of the desired gravity, usually 22° Bé. for syrup conversions, is run into a converter and cooked with live steam until the color reaction of a test sample drawn from the converter coincides with that of a similar sample tested in the laboratory and found of the desired degree of conversion or dextrose ratio. The operations of the converter are thus controlled directly by the laboratory. The charge, once having been brought to the desired test, is released into a neutralizer where sufficient sodium carbonate is added to neutralize exactly the hydrochloric acid in the syrup. The completeness of the neutralization is determined at frequent intervals, but cannot vary one way or the other more than a trifle for this reason: there still remains in the starch a minute amount of gluten after all the previous treatments and this is kept in solution in the hot slightly acid syrup. Once neutrality has been reached, this trace of gluten, carrying with it a trace of oil and pentosans, separates, causing a "break." At this

point the liquid can be filter-pressed and this residue removed, but either a trace of acid or of alkali prevents this; consequently, the neutralization in a way is fool-proof although there is a fine point of exact neutrality that can be determined only by laboratory tests.

In the manufacture of corn sugar, the operations are similar to the above excepting that the action is carried further, until from 85 to 95 per cent of the starch has been hydrolyzed, depending upon the kind of sugar. The neutralization and subsequent purification, however, are practically the same as with corn syrup.

The purification of the syrup is obtained by means of charred bone or bone-black and throughout the process until the refined and concentrated liquors are finished and ready for shipment great care must be taken to see that all conditions are the most favorable; that the gravities of the liquors are kept constant; that no contamination by dirt or entrance of wild yeast is allowed; in short, that all conditions are as ideal as possible. This is brought about by means of laboratory tests on average or special samples taken at all stages of the refining and finishing processes. In this way it is possible to detect and remedy trouble or irregularities, which, if allowed to persist, might affect the color or general appearance or even the quality of the finished product. For example, a leaking valve might allow raw starch to escape from the converter before it had had a chance to be hydrolyzed, but a test with iodine would reveal this. Or the sides of some of the tanks might become infected by wild yeast, but as tests would show this long before any real trouble could be experienced, the source of the irregularity is thus discovered and remedied. Thus by constant watchfulness and frequent tests it is possible to maintain uniformity and satisfactory operations in this most important department, but this eternal vigilance must not let up day or night.

The finished corn syrup is concentrated *in vacuo* to a gravity of 42, 43, 44 or 45° Bé. based on a temperature of 100° F. These gravities are taken at the vacuum pans, but samples taken to the laboratory serve as a check and keep the pan man lined up.

The gluten and the bran separated as already outlined are united, the concentrated soluble matter removed from the corn during the steeping added, and in due time we get corn gluten feed. The chief function of the laboratory in connection with this is to determine the moisture in the finished product, and thus keep the product up to standard in this respect.

The germ of the corn, removed in the first mechanical separation, is sent to the oil house where it is dried, ground, cooked and the oil expressed, the residue forming corn oil cake or corn oil cake meal as the case may be. A determination of the oil left in the cake or meal shows the satisfactory or unsatisfactory operation of the hydraulic presses or oil expellers.

In what has been said, account has been taken only of the material actually in process and recovered. It

is necessary, however, to look out for losses. These are sought in the sewers. Inasmuch as the milling process requires a great volume of water, it is necessary to get rid of this at various places. Wherever there is an outlet to the sewer a continuous automatic device is or should be placed and the samples tested for solids in suspension and solution. Solids in suspension are unnecessary loss and require immediate steps to remedy or obviate the condition permitting this. Solids in solution may indicate avoidable loss or a loss too small in amount or too diluted in quantity to recover. In the refinery there is possibility of entrainment during boiling in the vacuum pans and the slight amount of syrup which would be carried over can be detected and roughly estimated colorimetrically, if desired, by the use of the alpha naphthol test. Leaks in the steam tubes of the vacuum pans which might permit syrup to leak through when the vacuum is broken can be detected by this same test in samples of the condensed steam from the tubes. Similar tests will show whether the filter presses and the bone-black filters have been sweetened off properly before being washed to the sewer.

By making tests of these waters, day and night, a very accurate control is possible of the conditions in the refinery, and, in fact, in the whole plant, which might lead to avoidable losses.

SPECIAL METHODS AND TESTS.

In order properly to guide factory operations it will be seen that the laboratory must make many tests and that the results must be obtained in the shortest time conducive to a satisfactory degree of accuracy. This means that short-cuts and quick methods are required and that these shall give essential agreement with official methods. A few examples will illustrate:

Moisture determinations may be made in a vacuum bath heated by steam jacket at atmospheric pressure in three hours.

In determining oil in various products carbon tetrachloride may be used as an extractive reagent and the total time of extraction reduced to 2½ hours, the results agreeing very closely indeed with official results by ether extraction by the official method. This method has been used by the writer for many years and was described in the *Journal of the American Chemical Society*, 26 (1904), 568. Another advantage of this solvent is its freedom from danger of combustion. Starch may be determined indirectly by malting in the usual manner, filtering on weighed filters and determining the loss of weight after thorough drying. This loss of weight corrected for moisture and water-soluble matter in the original material for the insoluble solids in the malt extract used may be taken as starch and is perhaps as accurate as the official determination of starch by the reducing value of hydrolyzed malted extract, and the time consumed is much less.

Reducing value is determined volumetrically by a Fehling solution standardized by C. P. dextrose so

that 25 cc. solution is completely reduced by $12\frac{1}{2}$ cc. of 1 per cent dextrose solution.

Protein is determined by the modified Kjeldahl method using copper sulphate. Where practicable 0.875 g. material is taken and the final titration with $N/10$ alkali gives percentage directly, 1 cc. being equal to 1 per cent protein in the sample.

The above are the more important control tests, but special tests suggest themselves for special cases. Colorimetry plays an important part in comparing colors of starch, syrup, and other materials with standards. In controlling the strength of the weak sulphurous acid used for soaking the corn and testing for its subsequent removal, considerable amounts of iodine solution are required. Owing to the increasingly high cost of iodine and potassium iodide, the writer has been using for routine work a solution of potassium permanganate standardized through sulphur dioxide against iodine solution. This solution works admirably for control work and yields a marked saving in expense.

The results furnished by the laboratory show what is taking place at different steps of the process through the factory. These results, however, must be coördinated and applied in order to make them of value. From the results of the routine tests the foremen in the different departments of the plant can correct their respective operations so as to improve the results. At other times some unusual condition or combination of conditions may bring about unfavorable results, which will require special tests and analyses and perhaps more or less research work in order to avoid them. Once a certain kind of trouble has been experienced it becomes easy to avoid this a second time, but in the manufacture of cornstarch and corn syrup, as of course, in other industries, it is the unexpected that usually happens. Consequently, the one in charge of operations must not only keep in constant touch with the laboratory results, but carry on such additional tests and experiments as seem necessary in order to obtain the information which will permit getting the most satisfactory results from the plant.

EXAMINATION AND STANDARDIZATION OF FINISHED PRODUCTS.

A complete analysis of the different finished materials serves as a guide for standardization. For example, the gluten feed and corn oil cake meal must be guaranteed to contain not less than a stated minimum of protein and fat and not more than a stated maximum of fiber. These limits will naturally be put at such values that under the individual factory conditions they can always be attained unless for some very unusual cause. It is the function of the laboratory to prove whether or not these guarantees are met, although for that matter the process control will give a very definite idea as to this. The crude oil is analyzed for its content of free fatty acids: if the oil is refined, a still further control must be exercised,

both over process and finished product. The starch is tested for moisture and for impurities, which in this case are the other normal constituents of the corn, viz., protein, oil and fiber, which should be present in the merest trace. Corn syrup will be tested for gravity and perhaps acidity. It is interesting to note that pure corn syrup has a trace of acidity, using phenolphthalein as indicator, due apparently to some slight acidity of the dextrins or other inversion products formed in the hydrolysis of the starch. It also has a trace of alkalinity, using methyl orange as an indicator, due to traces of sodium phosphate present in the ash of the syrup. With rosolic acid as indicator, it is practically neutral. In addition the syrup may be tested for its boiling properties as used with sugar in candy making, and its resistance to discoloration when heated. This latter would be noticeably affected were the refining process insufficient to remove all but the most infinitesimal traces of gluten, etc. In short, it is the duty of the laboratory to devise and execute the most rigid and severe tests in order that the syrup may be brought to the very highest state of purity.

SPECIAL AND RESEARCH WORK.

No industry is in a really healthy condition unless it is advancing along the lines of improvement of its products or development of new fields for their use. In the starch and corn syrup industry there is still opportunity for abundant research work and there will be found many new uses for the products already made and many new products discovered which can be manufactured from the constituents of the corn kernel. The number of different products is already large, including pearl and powdered starch, various kinds of lump starches, modified starches, soluble starches, dextrins of various kinds, corn syrup, several preparations of corn sugar, refined oil for table uses, rubber substitute, cattle foods and many other products.

As regards improvements in quality, it may be said that the pure food law, which some ten years ago abolished the bleaching of corn syrup with sulphur dioxide, has been most beneficial as it necessitated improvements in the refining process so as to get a more highly refined product, and today corn syrup is whiter even than in the old days of bleaching syrup, and much better. In fact, it is one of the most, if not the most, highly purified food products that we have.

In conclusion we may repeat that the manufacture of cornstarch and corn syrup, while almost entirely a mechanical process in its execution, can be guided and controlled intelligently only by the most thorough, rigid and comprehensive system of chemical supervision.

During 1915 approximately 50,700 tons of ammonium sulphate was obtained from the coal-gas plants and about 197,000 tons from by-product coke plants, a total of about 198,000 tons. The value of this ammonia was more than \$11,175,000.

THE PROTECTION OF IRON BY ELECTRO-PLATING.*

By OLIVER P. WATTS and PAUL L. DEVERTER.

Although nickel-plated iron is satisfactory for use indoors, when exposed to the weather it almost invariably rusts. Brass-plated steel is extensively employed for the cheaper grades of builders' hardware, but is even more unsatisfactory than nickel plate for out of door use. In reply to an inquiry concerning the possibility of a durable brass plate on steel for use out of doors, The Metal Industry¹ says, "An electro-deposit of zinc on steel or iron is the only one that will withstand atmospheric conditions for any length of time, and a demand is now being made for hardware that has received an electro-deposit of zinc before being plated with any other metal for ornamental purposes, such as nickel, copper, brass or bronze. This double coating gives good service and is the only satisfactory one for hardware which is exposed to the weather."

The superior protective action of electro-galvanizing in comparison with deposits of other metals on iron is well recognized. This has generally been ascribed to voltaic action, whenever a hole is broken or worn through the plating a voltaic cell is formed between the metallic coating and the exposed iron. If the coating consists of a metal which is electro-positive to iron, the latter is cathode and is protected from corrosion, but if the coating is electro-negative to iron this becomes anode, and is corroded worse than if the "protective coating" were entirely absent. Examination of tables of potentials of the metals shows that, of the metals which can be satisfactorily plated out of aqueous solutions, only zinc and cadmium are electro-positive to iron. Since cadmium is not used for commercial plating on account of the expense, zinc remains as the only electroplate which can protect iron by voltaic or galvanic action. Theory and practice appear to be in harmony.

Galvanic action requires that two unlike conductors be in electrical connection with each other and with an electrolyte. So long as the iron is completely covered by the electroplate there is no opportunity for voltaic action, either corrosive or protective, and, so far as rusting of the iron is concerned, it is immaterial what metal constitutes the coating. The protection of iron by deposits of zinc and its universal rusting when plated with other metals seems to indicate either that electro-deposits of zinc are less porous than those of other metals, or that in the thickness used commercially all electro-deposits are porous, or on exposure soon become so, and thus the superior protection by zinc is due solely to its galvanic action.

The investigate the porosity of electroplating, and to determine the protection afforded to iron by de-

posits of different metals, a series of experiments has recently been carried out in the electro-chemical laboratory of the University, and it is thought that these are of sufficient interest to electroplaters to merit publication.

THE PROTECTION OF IRON BY DEPOSITS OF NICKEL, COPPER AND BRASS.

Since it is generally conceded that commercial plating with these metals does not protect iron from rust, it was decided to try much thicker deposits than those usually employed. A company which makes great quantities of an article in daily use by millions of people specifies ten milligrams of nickel per square inch as the minimum for good deposits, and fifteen for their heaviest plate. The latter corresponds to an average thickness of 0.00348 mm. or 0.000137 inches, and requires an hour at five amperes per square foot for its deposition. For indoor use this deposit stands well the constant handling to which these articles are subjected. The deposits of the tables which follow range from this thickness to ten and in a few cases even twenty times heavier.

Strips of sheet iron were pickled in sulphuric acid to remove scale, cleaned in the electric cleaner, dried, weighed, returned to the electric cleaner for a few seconds, rinsed, and hung in the plating bath. After

TABLE I.
Brass Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm. ²	Thickness Inches.	m.m.	Amp. Hrs./dm. ²	Cur. Eff. Per cent
1	55	Hot	11.5	0.00028	0.0071	1.0	26.7
2	10	Hot	11.5	0.00061	0.0155	1.9	30.1
4	15	Hot	12.3	0.0008	0.0203	3.07	25.5
6	30	Hot	12.6	0.00228	0.059	6.3	33.1
7	60	Hot	8.75	0.00327	0.0832	8.75	33.9
41	150	Hot	8.0	0.00607	0.1543	20.0	34.5

TABLE II.
Copper Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm. ²	Thickness Inches.	m.m.	Amp. Hrs./dm. ²	Cur. Eff. Per cent
36	3	Hot	7.32	0.00027	0.0069	.37	58.2
3	10	Hot	6.83	0.00096	0.0245	1.12	71.2
5	15	Hot	6.83	0.00099	0.0251	1.58	51.8
9	45	Hot	5.55	0.00129	0.0327	4.1	31.9
8	75	Hot	5.68	0.00271	0.0689	7.1	39.1
42	120	Hot	3.25	0.00248	0.063	6.5	33.1
46	180	Hot	3.27	0.00686	0.1745	9.81	60.8

TABLE III.
Zinc Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm. ²	Thickness Inches.	m.m.	Amp. Hrs./dm. ²	Cur. Eff. Per cent
21	4	Hot	4.88	0.00019	0.0049	0.32	71.6
19	1	Cold	14.7	0.000196	0.0050	0.24	97.4
14	3	Cold	13.25	0.00043	0.0109	0.66	85.3
10	5	Cold	13.65	0.00077	0.0195	1.14	86.2
11	12	Cold	12.5	0.00103	0.0263	2.3	63.1
13	30	Cold	9.55	0.00237	0.0603	4.77	60.5
12	25	Cold	14.7	0.00266	0.0667	6.1	52.0

TABLE IV.
Nickel Deposits on Iron.

No.	Time Min.	Temp.	Amp./dm. ²	Thickness Inches.	m.m.	Amp. Hrs./dm. ²	Cur. Eff. Per cent
30	20	Cold	1.3	0.00016	0.0042	0.43	45.5
25	10	Cold	2.3	0.00022	0.0055	0.4	51.0
31	15	Hot	4.85	0.00069	0.0176	1.2	78.5
33	30	Cold	1.0	0.00091	0.0231	1.5	62.5
29	20	Hot	5.28	0.00102	0.0255	1.76	72.0
32	25	Hot	6.48	0.00146	0.0371	2.7	63.5
34	40	Hot	7.2	0.00210	0.0633	4.8	55.0
44	180	Hot	4.23	0.00598	0.152	12.75	48.1
45	165	Hot	5.56	0.00702	0.178	15.95	42.7

*Paper presented at 30th General Meeting of the American Electrochemical Society, in New York City, Sept. 28-30, 1916.

¹Metal Industry, 1915 p. 469.

²Trans. Am. Electrochem. Soc. (1916) 29, 126.

plating the strips were reweighed, and the average thickness of the deposit calculated. The brass and copper deposits were made from hot cyanide baths containing caustic soda; the zinc solution consisted of the sulphate and a little chloride; the nickel was plated from a rapid solution recommended by the writer², which was used hot except for two samples. The conditions of deposition are given in Tables I to IV.

The samples were placed in wood racks, exposed to the weather, and examined occasionally for their appearance in regard to rust. The results are shown in Tables V to VIII.

The most striking feature of the weathering tests is the complete protection against rust during four months of very wet weather afforded by electro-galvanizing less than 0.0002 in. thick, while rusting occurred through deposits of copper 0.0027, of brass 0.00327, and of nickel 0.00102 in. in thickness. With thin plating rusting was serious and widely distributed, but on the thicker deposits it was confined to a few widely scattered spots. Although Nos. 42, 46 and 41 showed no signs of rust after seventy days' exposure, they had tarnished so badly that all resemblance to the original copper or brass was lost. Specimens Nos. 44 and 45 not only were free from rust, but the nickel plate appeared as bright as when deposited.

DOUBLE PLATING.

In addition to the quotation already cited in favor of a coating of zinc under brass or copper plating on iron, the current issue³ of The Metal Industry con-

tains the following: "Neither copper, brass or nickel gives a successful coating upon steel that will resist atmospheric influence and prevent the formation of rust. The large hardware manufacturing companies have realized these facts and are at the present time giving their product a preliminary coating of zinc from an alkaline cyanide zinc solution which is followed by direct deposition of copper, brass or nickel, or coating the zinc with copper or brass and then nickel plating. This method is the most effective for all purposes of plating upon steel when exposed to dampness or the action of salt air."

In view of such favorable reports from practical platers concerning the protective effect of a deposit of zinc beneath copper or brass plate, it was deemed advisable to test such double plating. Specimens were therefore prepared as shown in Table IX.

The results of weathering in Table X show slightly better protection by double plating than with the same total thickness of brass or copper alone; had the zinc deposits been free from blisters it is probable that the results would have been still more favorable to the double deposit. The final rusting of every sample of double plating is in marked contrast to the complete protection afforded by zinc alone.

The zinc in No. 17 is nearly as thick as in Nos. 19 and 21, which gave perfect protection. The result of covering the zinc in No. 17 with 0.003 in. of brass has been to nullify the protective action of the zinc and

³June, 1916.

RESULTS OF WEATHERING.

TABLE V.

Copper-plated Iron.

No.	Amp. Hrs./dm. ²	Thickness, Inches.	Days required for rusting.		
			Slight.	Mod. erate.	Very bad.
36	0.37	0.00027	8	10	14
3	1.12	0.00096	47	73	88
5	1.58	0.00099	47	73	88
9	4.1	0.00129	47	73	88
8	7.1	0.00271	67	88	..
42	6.5	0.00248	No rust in 70 days.		
46	9.81	0.00686	No rust in 70 days.		

Brass-plated Iron.

No.	Amp. Hrs./dm. ²	Thickness, Inches.	Days required for rusting.		
			Slight.	Mod. erate.	Very bad.
1	0.98	0.00023	20	32	73
2	1.9	0.00051	46	73	88
4	3.07	0.00066	47	73	88
6	6.3	0.00228	53	73	88
7	8.75	0.00327	53	73	88
41	20.0	0.00607	Tarnished, but no rust in 70 days.		

Nickel-plated Iron.

No.	Amp. Hrs./dm. ²	Thickness, Inches.	Days required for rusting.		
			Slight.	Mod. erate.	Very bad.
30	0.43	0.00017	9	19	40
25	0.4	0.00022	9	19	40
31	1.21	0.00069	12	19	53
33	1.5	0.00091	19	40	73
29	1.76	0.00102	19	40	73
32	2.7	0.00146	Tarnished, but no rust in 122 days.		
34	4.8	0.00249	Tarnished, but no rust in 122 days.		
44	12.75	0.00598	Bright, not even tarnished in 70 days.		
45	15.02	0.00702	Bright, not even tarnished in 70 days.		

TABLE VIII.

Zinc-plated Iron.

No samples rusted in 122 days.

TABLE IX.
Double Plating on Iron.

No.	Metal.	Time, Min.	Temp.	Amp./dm. ²	Thickness		Amp. Hr./dm. ²	Cur. Eff.
					Inches.	m.m.		
15	Zinc	3	Cold	14.35	0.00041	0.0104	0.72	70.2
	Copper	15	Hot	7.18	0.00107	0.0272	1.79	47.3
16	Zinc	1	Cold	12.95	0.00013	0.0034	0.21	86.3
	Copper	20	Hot	5.95	0.00145	0.0368	1.93	70.0
20	Zinc	3	Hot	4.88	0.00018	0.0045	0.24	87.3
	Copper	15	Hot	7.32	0.00119	0.0304	1.83	50.5
17	Zinc	1	Cold	13.85	0.000157	0.0040	0.23	85.8
	Brass	25	Hot	12.15	0.00327	0.0832	5.5	58.3
18	Zinc	3	Cold	12.27	0.00040	0.0102	0.61	85.6
	Brass	20	Hot	11.7	0.00186	0.0473	3.9	48.4

TABLE X.
Results of Weathering on Double Plating.

No.	Amp.	Hrs./dm. ²	Thickness	Days required for rusting.	
				Inches.	Days
17	0.23	Zinc	0.000157	53, slight;	70, six rust spots on one side.
	5.5	Brass	0.00327		
18	0.61	Zinc	0.00040	40, slight;	70, shows 25 rust spots.
	3.9	Brass	0.00186		
15	0.72	Zinc	0.00011	14, slight;	70, much rusted.
	1.79	Copper	0.00107		
16	0.21	Zinc	0.00013	20, slight;	Zinc blistered and broken in 70 days, rusted in such spots
	1.98	Copper	0.00145		
20	0.20	Zinc	0.00018	14, slight;	70, many blisters and rust spots.
	1.83	Copper	0.00012		
35	0.33	Zinc	0.00019*	73, slight;	122, eight rust spots.
	0.92	Copper	0.00062		
35a	0.33	Zinc	0.00019*	53, slight.	
	0.92	Copper	0.00062		

*As the weights of these samples were not recorded the thickness of the deposits have been computed from the ampere hours by comparison with other deposits.

to induce rusting at nearly the same rate as Nos. 6 and 7, which were without the coating of zinc. A detailed comparison of the other double deposits with the single coatings leads to a similar conclusion: the protective effect of the zinc coating is almost, if not completely, nullified by plating it over with brass or copper. The reason for this is easily seen. Zinc protects by galvanic action at the expense of being itself corroded. (It should be noted that the relative size of the surfaces of the two metals is a factor of tremendous importance in determining the extent of the corrosion or protection of one metal by contact with another.) In No. 19 the surface is zinc, with here and there a pin-hole exposing a minute bit of iron. The corrosion of zinc necessary to protect these microscopic surfaces of iron is so small in amount, and is applied to so large a surface of zinc, that a deposit of the latter only 0.0002 in. (0.005 mm.) thick can protect the iron for months, if not for years, against ordinary atmospheric corrosion. In No. 20 such a deposit of zinc has been copper plated, with here and there a pin-hole through which the zinc is exposed. (The iron may or may not be exposed—the results as regards rusting will be the same.) Each pin-point of exposed zinc plate is surrounded by a relatively enormous surface of copper cathode, and in its endeavor to protect the copper against corrosion and tarnish the zinc is soon entirely dissolved, exposing the iron beneath it. This, like the zinc, acts as anode toward copper, and rusting is the result. Such a sub-coating of zinc can at best only slightly delay the rusting of iron plated with brass, copper, nickel, etc. If this practice is to be followed the zinc deposit should be made as thick as possible, in order to lengthen its life when once it is exposed and begins to act as anode. What is needed is a non-porous coating of nickel, brass or copper. Whether or not this can be obtained without going to the extreme thickness found necessary in these experiments is for someone of wider experience than the writer to say.

POROSITY OF ELECTRO-DEPOSITS.

The prompt rusting of the iron beneath the thinner deposits of all the metals except zinc seemed to indicate either that such deposits are porous in structure, or that there are small holes at certain points which leave the iron exposed. To study this question use was made of an ingenious, yet simple, method employed by W. H. Walker for detecting holes in tin plate.

A one and a half per cent solution of agar was prepared, and to each hundred cubic centimeters of this 7 cc. of a 1 per cent solution of potassium ferrocyanide was added. The samples of plated iron were placed in a shallow glass dish and covered with the hot solution, which quickly set to a stiff jelly. In a short time numerous blue spots appeared on the thinner deposits.

With copper-plated iron the action is as follows: whenever there is a crack or hole in the plating a gal-

vanic cell is formed in which the exposed iron is anode, goes into solution in the ferrous state, and is precipitated as Turnbull's blue, just as when a solution of potassium ferrocyanide is added to the solution of a ferrous salt in a test tube.

The results of this test are shown in Table XI. As these deposits were not weighed their thickness can only be estimated by a comparison of the ampere hours per square decimeter with those of Tables I, II and IV.

All of the deposits were found to contain pin-holes with the exception of the brasses, but unfortunately no deposits of brass less than 0.55 ampere hours per square decimeter were prepared for this test. Copper coatings up to 0.47 and nickel up to 1.81 ampere hours per square decimeter contained pin-holes, but thicker deposits were free from them.

The remarkable protection afforded by very thin deposits of zinc must be due entirely to galvanic action, unless zinc coatings are free from the holes which have been shown to exist in thin deposits of all other metals tried in these experiments. The ferro-cyanide test cannot be applied to zinc coatings, however, since any exposed iron would be cathode, therefore would not dissolve, and so would not make its presence known by the blue precipitate. A test for the detection of pin-holes in electro-galvanizing, for which we are also indebted to Prof. Walker, consists in immersing the strips of galvanized iron in a hot, strong solution of sodium hydroxide; wherever a bit of iron is exposed it becomes the cathode of a voltaic cell, and hydrogen is evolved from it. The results of these tests are given in Table XII.

TABLE XI.
Ferroxyl Test for Porosity.

Deposit.	Time, min.	Temp.	Amp./dm. ²	Hrs./dm. ²	Blue-spots.
Copper	1	Hot	5.5	0.09	Several
Copper	3	Hot	4.8	0.24	Few
Copper	5	Hot	5.6	0.47	None
Copper	10	Hot	5.6	0.94	None
Copper	20	Hot	5.9	1.99	None
Copper	40	Hot	5.9	3.91	None
Nickel	3	Hot	5.0	0.25	Many
Nickel	5	Hot	5.0	0.41	Many
Nickel	10	Hot	5.3	0.90	Many
Nickel	20	Hot	5.4	1.81	None
Nickel	40	Hot	5.1	3.4	None
Brass	3	Hot	11.1	0.55	None
Brass	5	Hot	10.4	0.87	None
Brass	10	Hot	11.8	1.96	None
Brass	20	Hot	11.8	3.93	None
Brass	40	Hot	11.3	5.65	None

TABLE XII.
Porosity of Zinc Deposits by Sodium Hydroxide.

Deposit.	Time, Min.	Temp.	Amp./dm. ²	Hrs./dm. ²	porosity.
Zinc	1	Cold	12.1	0.20	Many
Zinc	3	Cold	16.6	0.83	Many
Zinc	5	Cold	11.8	0.98	Few
Zinc	10	Cold	9.1	1.52	None
Zinc	20	Cold	10.0	3.33	None

TABLE XIII.
Porosity of Zinc Deposited on Aluminum.

Time, min.	Temp.	Amp./dm. ²	Hrs./dm. ²	Holes.
5	Cold	6.32	0.52	Many
10	Cold	6.57	1.09	Few
20	Cold	5.55	1.85	None
30	Cold	5.12	2.56	None

Thin zinc deposits proved to be as full of holes as were the coatings of other metals, and the freedom from rusting of lightly electro-galvanized iron is due solely to galvanic action. Deposits thicker than 1.5 ampere hours per square decimeter (14 amp. hrs./ft.²) were free from holes.

PIN-HOLES BY INSPECTION.

Another method of testing for porosity consisted in examining the electro-deposits by transmitted light. To secure zinc deposits advantage was taken of the poor adhesion of electroplating on aluminum. Sheets of aluminum were polished, immersed for a few seconds in the electric cleaner, rinsed, and plated with zinc. The edges of the sheet were then cut away, and the deposit was stripped off and examined. The results are given in Table XIII.

At and above 1.8 ampere hours per square decimeter no holes were found—a good agreement with the previous test.

The lack of adhesion of electroplating on aluminum is due, in part at least, to an invisible film of oxide on the surface of the metal, and in spite of the good agreement seen in the last two sets of tests, there remained a suspicion that this film of oxide might cause electroplating on aluminum to be less uniform than on other metals. It was therefore decided to avoid the use of aluminum for receiving the deposit, wherever possible. Nickel, copper, and brass deposits were obtained by plating on zinc, and dissolving this in dilute sulphuric acid. A description of the deposits and the results of inspection are shown in Table XIV.

This study of the porosity of electroplating seems to show that brass (0.000154 in. (0.0039 mm.) thick) and copper (0.000347 in. (0.0087 mm.) thick) deposits from the cyanide solution up to 0.5 ampere hours per square decimeter (4.6 amp. hrs. / ft.²) contain pin-holes, and that nickel plating requires 1.5 ampere hours per square decimeter (14 amp. hrs. / ft.², 0.00102 in. thick) before pin-holes disappear.

In weathering tests of two to four months' duration, rusting occurred on brass and copper plate many times thicker than the minimum for the disappearance of pin-holes. In case of the heavier deposits rusting was confined to spots a millimeter or less in diameter,

the spaces between spots giving perfect protection to the iron beneath. For nickel plate there was good agreement between the disappearance of holes and freedom from rust. The divergence shown in this respect by copper and brass plating may possibly be due to the greater difference of potential between these metals and iron than that which exists between nickel and iron. The greater the difference of potential or corrosive force, the more difficult will it be to prevent rusting. For copper deposits there were no holes at 4.4 ampere hours per square foot (0.000347 in., 0.0087 mm., thick) and no rusting at 60.4 ampere hours per square foot (0.00248 in., 0.062 mm., thick). Similar values for brass plate are 5.1 amp. hrs. / ft.² (0.000154 in., 0.0039 mm.) for no holes, and 20 amp. hrs. / ft.² (0.00607 in., 0.152 mm.) for no rusting. Nickel required 16.8 amp. hrs. / ft.² (0.00108 in., 0.027 mm.) for the absence of holes, and 25.4 amp. hrs. / ft.² (0.00146 in., 0.037 mm.) for freedom from rust.

The only hope of a general use of copper and brass plate on iron exposed to the weather seems to lie in securing a uniform deposit, free from pin-holes. In special cases it may be feasible to employ the extremely thick deposits of these metals which have been shown to be necessary to protect iron from the weather, but unless the plated article is fairly rigid there is danger of cracking and peeling of such heavy deposits, and the time and expense of producing them will prevent their general employment.

CONCLUSIONS.

1. These experiments confirm the orthodox view that the superiority of electro-galvanizing over deposits of other metals for the protection of iron is due to voltaic action.

2. It has been shown that thin electro-deposits of zinc, copper, nickel and brass are full of holes, and therefore only the first may be relied on to prevent rusting, unless deposits are made much heavier than is at present the rule.

3. Deposits of nickel should exceed 0.0015 in. (0.038 mm.) in thickness in order to protect iron out of doors, and copper or brass plate should have three times this thickness. Even then it is a question how long such coatings will afford protection.

4. For the protection by electroplating of iron which is to be exposed to the weather, zinc (or cadmium) is the only metal worthy of consideration.

5. The foregoing experiments do not show that double coatings—zinc followed by copper or brass—are distinctly superior to a single heavy coating of the latter metals. If zinc is to be used advantageously, it should form the outer coating.

6. It is very desirable that some method be found for producing a uniform electroplate, free from the holes which were responsible for rusting in these experiments. Could such plating be done deposits of nickel, copper and brass would form a far more effective protection to iron than at present.

TABLE XIV.
Porosity of Metal Deposits on Zinc.

Deposit	Time, min.	Temp.	Amp./dm. ²	Hrs./dm. ²	Amp. Hrs./ft. ²	Holes.
Copper	3	Hot	8.2	0.41	0.000154	Few
Copper	6	Hot	6.1	0.61	0.000347	None
Copper	6	Hot	6.8	1.14	0.000607	Few
Copper	10	Hot	7.5	1.20	0.00087	None
Copper	20	Hot	6.5	2.18	0.00174	Few—6 per sq. in.
Copper	40	Hot	7.8	3.12	0.00347	Few—4 per sq. in.
Brass	3	Hot	12.0	0.60	0.000154	None
Brass	5	Hot	12.0	1.0	0.00026	None
Brass	10	Hot	12.0	2.0	0.00052	None
Brass	20	Hot	12.0	4.0	0.00104	None
Nickel	3	Hot	9.2	0.46	0.000154	Many
Nickel	5	Hot	9.5	0.79	0.00026	Many
Nickel	10	Hot	9.0	1.50	0.00052	Several
Nickel	20	Hot	12.9	4.30	0.00104	None
Nickel	40	Hot	12.9	8.60	0.00208	None

THE CHEMICAL CONTROL OF GELATINE MANUFACTURE.*

By J. R. POWELL†

Previous to the present decade, chemical control in the gelatine industry was rather limited. The manufacturer bothered himself chiefly about producing a product that would give a sufficiently strong jelly, and be brilliant enough in appearance to satisfy a trade which was critical about these points only. With the recent awakening to the possibilities of better manufacture and control of all food products, a more exacting chemical control of gelatine manufacture became a commercial necessity. Once this control was established, it became, and still is, proving of real assistance to the manufacturer, in addition to developing a product acceptable to the trade. Improved methods introduced have tended to increase yields, improve what is commercially known as test, and conserve by-products, all of which gives the producer greater returns. As a result, what was once looked upon as a necessary nuisance will soon come to be accepted as a necessary source of help.

However, in outlining the precautions taken in this industry, many things will be mentioned under chemical control, that, while properly so designated, are the outgrowth of long practical experience, and cannot be directly credited to the introduction of chemistry. It is remarkable, however, as others have undoubtedly noticed in other industries, how many processes or tests practical men sometimes use, which, on first inspection, seem to be without rhyme or reason, are found to be based on very sound principles, when given a thorough study.

Control work naturally divides itself into three classes: (1) Inspection of raw materials and chemicals, (2) control of the manufacturing process, (3) inspection of the finished product.

RAW MATERIALS AND CHEMICALS.

Raw materials for the manufacture of gelatine, being by-products of other industries, have been far from being standardized, and the quality has been extremely variable. When the supply of materials was great, corresponding to the demand, and as a consequence, the price was correspondingly low, this variation did not worry the manufacturer so much. Margins were great enough that some variation in yield could be overlooked. As the demand for this material comes to exceed the supply, and it becomes necessary to buy on a competitive basis, the possible yield from such material becomes a vital point. As a result, inspection of such material for its actual value to the manufacturer is continually becoming more important. If the stock is to be used only for glue manufacture, examination ends at this point, but that used for the manufacture of gelatine should be exam-

ined for impurities that would render it unfit for making an edible product. For instance, arsenic and other heavy metals that are not permissible in the finished gelatine may be present in such quantities that the stock cannot be used, so it must be turned to the manufacture of glue or technical gelatine. Other stock may contain only such impurities as can be removed by proper processing, and subsequent treatment must, at least in part, depend upon the results of the examination. Still other stock may be found that shows no impurities and may be processed without any such special provisions being made.

In the examination of chemicals, it is such impurities as just mentioned that require the greater attention, as most of these products have been standardized, and variations in quality are limited. It is easy to conceive how acid used in the process may contain objectionable quantities of the tabooed metals. Water is so common that it is not usually considered a chemical, but in certain manufacturing processes would rightly be considered as such. Although at first thought it seems easy to obtain a water supply that is free from objectionable impurities, it would be interesting to consider the effect the total solids in a water of ordinary purity would have on a finished product, when this water is used for boiling out the gelatine. Gelatine liquor leaves the boiling vats at a concentration of from 2 to 3 per cent. If the water in question contained 15 grains of total solids as mineral matter per gallon, this would add about 1 per cent of an ash in the dry gelatine obtained to that extracted from the stock and coming from the other sources.

MANUFACTURING PROCESSES.

The chemical control of the various processes of manufacturing can be made very elaborate. For the sake of economical and convenient operation, however, this control work usually is, as far as possible, worked out to a system of simple tests that can be made by the operators who handle the routine of the manufacture. These operators may not understand the mechanism of the tests, or know what they are really testing for, but are trained to expect certain reactions, and if they do not obtain them, they know all is not well, and the attention of the proper party may be called to the trouble.

This control of the manufacturing process begins with the first treatment of the raw material, which is usually the so-called liming. As this is usually conducted in a saturated solution of lime-water, the strength of the solution requires no control. On the other hand, the stock must be well watched, as over-liming will reduce the yields very materially, while under-liming will likely leave behind certain impurities that should be removed, and, at the same time, require such drastic treatment in boiling that the test will be decidedly injured.

Following the liming comes the washing, wherein the excesses of alkali must be removed to within certain limits, together with other impurities that the

*From The Journal of Industrial and Engineering Chemistry.
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lime has dissolved. As it is usually customary to boil slightly acid, this is usually followed by an acid wash, which neutralizes the residual alkali and gives the required acidity. It can be readily seen that, without some control, large amounts of acid may be wasted, unnecessary time and labor consumed in washing, or impurities left behind that should be removed.

The boiling of the stock follows the proper preparation in the wash-mills. The chemical control here is rather limited, the points of interest being chiefly the reaction and the temperatures. High temperature and excessive acidity or alkalinity rapidly hydrolyze gelatine into products of considerably less value.

From this point on through the process, the chemical control diminishes in importance, unless the liquors are to be clarified, or subjected to some other treatment for removal of impurities. However, as the importance of this control decreases, the importance of bacteriological control increases. This is another type of control which will be but mentioned here, that offers a very wide field of application to all points in the manufacture of gelatine, and the possibilities of which we are just beginning to appreciate. But it is especially while gelatine is in these comparatively dilute solutions, and varying in temperature from boiling through an ideal incubating state to the necessary refrigeration required for its congealing, it becomes an ideal breeding place for bacteria. Hence all possible precautions must be taken to prevent infection and get the material past the danger stage as rapidly as possible.

Another item of importance is the air used in the drying of the gelatine. This is especially so where the air must be drawn from the badly polluted atmosphere of our larger cities. Impure air offers three possibilities: First, the dirt that may be collected, giving a gelatine that will dissolve with great turbidity; second, infections are frequent picked up in the drying alleys, from this dirt, although the product may have entered them practically sterile; third, the chemical contamination due to the absorption of chemical fumes in the air.

As has been mentioned, one of the points that must be carefully watched is the reaction of the material throughout the process; and to see how far-reaching the effects of any one factor might be, we will consider this more in detail.

The well-known influence of acidity on the swelling of gelatine and like colloids points to the importance of such control. The points of maximum and minimum swelling of the stock must be definitely related to the extraction of the gelatine and the properties of the resulting product. The fact that salts again modify this action of acidity only adds other complicating factors. The possible detrimental hydrolyzing action of acid or alkali has already been mentioned. Although the process of boiling out of the gelatine is most probably one of hydrolysis, it must be done under such control as will insure the action

going only so far, or the product is deteriorated.

Likewise the wonderful probabilities for the formation of undesirable precipitates must be considered. We may have almost any combination of acid, or alkaline albuminates, mucins, and such substances, together with the inorganic compounds, especially the uncertain phosphates. There are conditions where a very slight change in acidity may bring down any one of these, or more likely, a combination of several. Much work has been done on the preparation of colloidal precipitates along other lines, and the operators have gone to great pains and trouble to obtain such precipitates. Here the conditions are somewhat reversed, and great care must be taken to avoid the formation of precipitates in the colloidal state. One of the great factors in this is that gelatine is a protective colloid, and the tendency is for all precipitates to separate in the colloidal form. This is the case even when precipitation is intentionally produced under careful control, for purification or clarification, making it easier, in most cases, to keep impurities out, rather than to attempt to remove them.

Besides the principal product, gelatine, the by-products must also be considered, and given their proper attention. There may be, depending upon the nature of the stock, a recovery of more or less fat, which is to be properly collected and graded. There will be the residual tankage which has its definite value as fertilizer, which valuation must be made on suitable analysis.

THE FINISHED PRODUCT.

Any control work done on the finished product simply amounts to such analytical work as is necessary to check up the work previously done during the process of manufacturing. Physical tests such as the rigidity of jelly, the viscosity of a solution, together with the appearance of the product gives data upon which the commercial value is fixed. Besides this, of course, the impurities must be checked up to show its suitability for edible purposes. Frequently, other special tests are demanded, depending upon the use to which the gelatine is to be put, but each case of this sort is a law unto itself, these tests being the outgrowth of some special demand made by the consumer.

According to a report on rubber production in South India recently prepared by the Department of Agriculture of the Madras Presidency the total area under Hevea rubber in 1914 in Cochin, Travancore, Malabar, Madras Presidency, and Coorg was 44,125 acres. The yield in Cochin was estimated at 334,000 pounds; Travancore, 1,985,469 pounds; Malabar, 103,400 pounds. No estimates of yield are given for the Madras Presidency and Coorg. The area under Ceara rubber (*Manihot Glazovii*) at the present date is stated in the report to be 12,000 acres in Coorg, 300 acres in Mysore, and 200 acres in the Shevaroy Hills.

SOUTHERN IRON ORES AS A SOURCE OF POTASH.*

By JOHN SHARSHALL GRASTY, PH.D., Sc.D., MINING GEOLOGIST.

The cutting off of the German potash supply has naturally directed attention in this country toward the possibility of obtaining potash from domestic sources. It has long been known that potash occurs in the gases given off by blast furnaces in the manufacture of pig-iron and from the kilns used in the manufacture of Portland cement, but it is only recently that the possibility of recovering potash from these gases has been seriously considered. The fact that it is possible to recover potash from these sources in commercial quantities seems now to be fully established, and the Security Cement & Lime Co., one of the pioneers in this field, has already erected a "treater" plant especially designed for this purpose. The process employed is in accordance with patents taken out by F. G. Cottrell, the principle being to pass the gases from the kilns through a series of tubes having high electric discharge. The effect of this is to precipitate very completely all particles of solid material carried by the gases, and the gases are thus cleansed and the potash recovered as a valuable by-product.

There is no reason why the Cottrell process cannot also be applied to the precipitation of dust carried by the gases from blast furnaces. As it has not yet been applied to these operations, there would, of course, be certain problems to be worked out; but it is the opinion of Mr. J. J. Porter of Hagerstown, Md., general manager of the Security Cement & Lime Co., who is also an experienced furnaceman, that it should not be as difficult to recover potash as a by-product from a furnace operation as from the kilns of a cement plant. Furthermore, in addition to the recovery of potash, possibly other valuable minerals such as zinc, etc., contained in the gases in finely divided state would no longer largely go to waste, but thus be saved as paying by-products. The introduction of the Cottrell process to recover potash, zinc, etc., from furnace gases would have the further advantage of giving clean gas for use in stoves and boilers. It is estimated roughly that a "treater" plant suitable for taking care of the gases from a 150-ton furnace would cost approximately \$75,000, if no especial effort were made to rush it to completion. If, though, a special effort were made to complete it promptly so as to take advantage of present prices, Mr. Porter, who has assembled a great deal of cost data on the erection of these "treater" plants, is of the opinion that the cost would probably be in the neighborhood of \$100,000.

The amount of potash to be recovered at any given furnace operation as a by-product would, of course, depend upon the composition of the raw materials employed. The calcareous raw materials, for instance,

made use of in the manufacture of Portland cement by the Security Cement & Lime Co. average about 1 per cent of potash (K_2O). These beds of limestone, according to analyses reported by Mr. Porter, vary all the way from 0.50 per cent up to 1.40 per cent, and the potash follows the impurities in the stone quite closely. A high-grade fluxing stone could not be expected, therefore, to carry as much potash as a stone more or less argillaceous in its nature. The more argillaceous or shaly the limestones (and these, by the way, would not be adapted for use as fluxing stone, though suitable for the manufacture of Portland cement), the more potash they would probably be found to carry. This is indicated by analyses on the material used at the plant of the Security Cement & Lime Co., where, for instance, the shale runs over 3 per cent potash, or is about six times as high in potash as the purer grades of limestone.

Some time ago Mr. Porter stated in a letter to the writer that his company expected, by the use of the Cottrell process, to recover about three tons per day of water-soluble potash (K_2O), which, according to the range in recent prices, is quoted at from \$300 to \$700 per ton. As the cost of production in this plant will, according to figures submitted to the writer, probably be less than \$10 a ton, obviously this by-product will contribute largely to the earnings of the company, and since the same process is well adapted for use in recovering potash from the gases of blast furnaces making pig-iron, it will also in the latter instance be a source of large profit. However, the amount of potash that would be recovered would depend upon the amount of potash carried by the ore, coke and limestone. If ores high in potash be available, obviously the yield will be accordingly larger and the "treater" plant correspondingly more profitable.

It is reported that a number of blast furnaces are selling their flue dust for its potash content without having made any attempt to recover from the furnace gases the maximum amount of potash. In this connection it may be noted that the Security Cement & Lime Co., prior to the installation of its potash recovery plant, sold the dust that collected at the base of the stacks. This dust averaged about $3\frac{1}{2}$ per cent soluble potash, and was sold to fertilizer manufacturers for \$2.50 per unit K_2O . It would seem obvious, therefore, that if the Cottrell process can make a commercial recovery of potash as a by-product in the manufacture of Portland cement, it has great possibilities if employed to recover potash, etc., at blast furnaces. As has been previously stated, however, the commercial possibilities of the recovery of potash both at cement and furnace plants are, of course, absolutely dependent upon the potash content of the raw materials. One of these materials, which, by reason of its potash content suggests itself for use in connection with the manufacture of Portland cement, is ortho-

*From The Manufacturers Record.

clase or potash feldspar, which, when pure, has the following composition:

Silica	64.7	per cent.
Alumina	18.4	per cent.
Potash	16.90	per cent.

Unfortunately, however, the proportion of silica to alumina in this potash-bearing feldspar is such that its use in "the mix" in the manufacture of Portland cement is limited both on this account and by the chemical composition of the limestone and shale employed and their ratios of silica, alumina and iron. However, there is no doubt that it can be introduced into the regular "mix" to great advantage in certain instances, and thus considerably increase the yield of potash in the "treater" plant, while its silica and alumina would combine with the other necessary ingredients which go to make Portland cement.

In view of what has been accomplished in the matter of recovering potash as a by-product in the manufacture of Portland cement, and the fact that the same process can be applied to the recovery of potash as a by-product in the manufacture of pig-iron, an investigation of the Southern iron ores with respect to their potash content was undertaken at the request of the editor of the *Manufacturers Record*. All analyses of the Southern iron ores that could be obtained, amounting to 1784 in all, were examined by the writer's engineer, Mr. F. B. Speed, Jr., with the following results:

Analyses showing
determination of

State.	Analyses examined.	potash.
Virginia	95	12
Georgia	151	0
Alabama	649	6
Tennessee	170	0
Mississippi	47	0
North Carolina	397	4
South Carolina	13	0
West Virginia	90	0
Kentucky	172	170
	1,784	192

The iron ores of Kentucky, it will be observed, are the only ones which show the determination of potash to any extent. At the present time these Kentucky ores are of subordinate commercial importance as compared with the ores of Alabama, Virginia, Georgia, Tennessee and North Carolina. It will be noted in referring to the above table that no determinations were made for potash on the Virginia or Tennessee ores. There were, then, but 22 determinations made on the more important Southern iron ores. From the figures given above it is evident, therefore, that little is known about the potash content of many of the more largely worked of these iron-ore occurrences. Probably the district in which potash content in iron ores has been more completely investigated—but even then not as thoroughly as it might be—is the Gray ore district of Talladega county, Alabama. In view of the possibilities offered in the recovery of potash as a by-product in ironmaking, it would certainly seem that a further investigation of the commercially important iron ores elsewhere would be well worth while and should be undertaken at once.

With regard to the presence of potash in iron ores, the observations on this subject made in a report* by Edwin C. Eckel, formerly chief of the Iron Ore Division, United States Geological Survey, are particularly interesting at the present time, when ores containing potash have a special value. It will be observed from the quotation from this report which follows that Mr. Eckel, while not pointing out the possibility of the recovery of potash as a by-product—which, of course, he could not do, as at that time (1907) the process for doing so had not been perfected—calls attention to the metallurgical advantages of its presence. He says:

Presence of Potash in Gray Ores.—A certain amount of criticism of the gray ore has been based on their assumed potash contents. This criticism may be regarded as due to ignorance on the part of the critics of the facts of the case. The conditions to be considered are as follows:

(1) The gray ores do not in general show high percentages of potash.

(2) Potash in small quantities is rather a benefit than a detriment.

(3) Many well-known American ores carry much more potash than the Talladega ores.

These conditions may be taken up in turn.

As to the percentage of potash actually carried by the average gray ore little is known, but it will probably fall under half of 1 per cent. The only recorded analyses in which potash determinations were made are as below:

Potash and Soda.	Locality.
1 1.95 per cent.	Mesaba Mine.
2 1.57 per cent.	Emauhee Mine.
3 2.11 per cent.	Emauhee Mine.

As to the effects of potash in the furnace, it may be said that:

(1) If present in excess, and not allowed for in proportioning the burden, potash will attack the furnace-lining. This effect would probably not be noticeable unless the potash in the total mixture was over 3 per cent.

(2) It is a strong fluxing agent, and will neutralize in certain percentages of the silica contained in the ore, acting as well in this respect as considerably larger percentages of limestone. In ordinary quantities, therefore, potash will aid in the slagging of the burden.

(3) Potash is a very efficient desulphurizer, being better in this respect than either lime or magnesia.

From the above summaries of the effects of potash in the furnace, it will be seen that it can be regarded as beneficial rather than detrimental when present in such small quantities as in the Talladega gray ores.

The same conclusion as to the effects of potash could be reached by considering the following table, which gives the potash and soda percentages in a number of well-known American ores. These analyses are quoted from official reports, and the analytical work, done by Blair, Whitfield, Gooch and King, was beyond question.

Alkali Percentages in Some American Ores.

No.	Potash.	Soda.	Total.	Kind of Ore.	Locality.
1	0.70	0.41	1.14	Brown Hematite.	Salisbury, Conn.
					Quinnisee Mine.
2	0.99	0.02	1.01	Specular Hematite.	Menominee Range, Mich.
					Cornell Mine.
3	1.54	0.17	1.71	Specular Hematite.	Menominee Range, Mich.
					Cornell Mine.
4	2.29	0.30	2.59	Specular Hematite.	Menominee Range, Mich.
					Keystone Mine.
5	0.92	0.86	1.78	Magnetite.	Marquette Range, Mich.
6	1.47	0.10	1.57	Brown Hematite.	Beattyestown, N. J.
7	1.13	0.34	1.47	Brown Hematite.	Amenia, N. Y.
8	1.80	0.17	1.97	Specular Hematite.	Wolf Creek, Tenn.
9	0.99	0.14	1.13	Magnetite.	Riverville, Va.

All of the above ores are from well-known mines, and all have been largely used and favorably known in our blast-furnace practice. In view of these facts, it seems ridiculous to criticize the Talladega gray hematite in this respect.

A comparison of the potash content of the gray ore of Alabama with other Southern ore occurrences brings out the fact that it appears to lead all others in this respect. However, the data as to potash content in other Southern ore occurrences is so incomplete that at the present time this comparison, which is so advantageous to the gray ore, hardly seems to be justified. The analyses on the ore occurrences quoted by Eckel in the above table, giving the alkali percentages in some American ores, indicate that potash in quantities ranging from .070 to 2.29 are not at all unusual; and hence it may be anticipated that many of the Southern ores will be found to contain around 1 per cent potash, as is contained, for instance, in the raw material employed by the Security Cement & Lime Co. If, therefore, the "treater" plant of the Security Cement & Lime Co. proves successful, which Mr. J. J. Porter, the manager of the company, anticipates will be the case, then it will be definitely demonstrated that the same process applied to blast furnaces would also pay, and as a result the iron industry of America will make this country more or less industrially independent of Germany, in so far as our supply of potash is concerned. The possibilities involved are enormous and are of such a nature as to justify a full investigation of all materials employed by blast furnaces to determine the question of the possibilities alluded to, which are fraught with such unusually attractive potentialities.

AN IMPROVED METHOD FOR THE DETECTION OF ARACHIDIC ACID.*

By ROBERT H. KERR.†

The method described below for the detection of arachidic acid in peanut oil and mixtures of oils containing peanut oil has been found to offer certain advantages over the Renard method adopted by the Association of Official Agricultural Chemists. These advantages consist in greater convenience, lessening of the number of operations, reducing the amount of attention required, and avoidance of the use of ether.

REAGENTS.

Potassium Hydroxide Solution.—Dissolve 100 g. of stick potassium hydroxide in 100 cc. of water.

Magnesium Acetate Solution.—Dissolve 10 g. of magnesium acetate in a mixture of 100 cc. distilled water and 100 cc. of 95 per cent alcohol.

Acetic Acid Solution.—Mix 50 cc. glacial acetic acid with 150 cc. of 95 per cent ethyl alcohol.

Sulphuric Acid Solution.—Mix 50 cc. concentrated sulphuric acid with 150 cc. of distilled water.

90 per cent Ethyl Alcohol (by volume).

METHOD.

Weigh out 20 g. of the oil to be tested in a 300 cc. Erlenmeyer flask, pour in 200 cc. of 95 per cent ethyl

alcohol, and heat to boiling on the steam bath. When the alcohol is boiling add 10 cc. of the potassium hydroxide solution. Saponification begins immediately and is soon complete. After the saponification has been completed add a few drops of phenolphthalein and neutralize the excess alkali with the alcoholic solution of acetic acid. Next add 50 cc. of the 5 per cent magnesium acetate solution and heat the whole mixture to boiling. Allow to cool to room temperature with occasional shaking and then place in a refrigerator at a temperature of 10 to 15° C. and leave until next day. Filter off the solution, wash the precipitate twice with 50 per cent alcohol and three times with distilled water, and return to the flask in which precipitation took place. Pour 100 cc. of hot distilled water into the flask and add sufficient dilute sulphuric acid to decompose the magnesium salts. Heat until the separated acids form a clear layer. Cool the flask, pour off the acid solution, add 100 cc. of hot water. When the fatty acids have melted and solidified, pour off water as before. Free the cake of acids of water as far as possible by draining; dissolve in 100 cc. of 90 per cent alcohol and separate the arachidic acid by crystallization, according to the present provisional method of the Association of Official Agricultural Chemists as given in Bulletin 107, Revised, Bureau of Chemistry, p. 146.

The method as outlined above has been used on a number of samples of peanut oil and mixtures of peanut and other vegetable oils. The results obtained are qualitative only, no attempt having been made to apply the method for quantitative purposes. It has been found to be capable of detecting 5 per cent of peanut oil in olive oil, cottonseed oil, soy bean oil and corn oil. These results are quite as good as the best which have ever been obtained with Renard's method.

Americans to Make Calcium Carbide in Norway.

American capital is employed in building a factory for the production of calcium carbide at Saude in the district of Stavanger, Norway, where there are falls suitable for the generation of large amounts of electrical power. Other electrochemical products are to be turned out by this factory for shipment to New York and sale in the American market. First shipments should be ready early in 1918, as the contract calls for the finishing of the plant by January 1 of that year. The new company is registered in Canada, and is called the Electric Furnace Products Co. (Ltd.). Edgar F. Price, an officer of the Union Carbide Co., of New York, is president of the organization. The power for the factory is to be supplied by "Saude-faldene" (The Saude Falls Co.), a Norwegian corporation financed by Norwegian capital. A lease of 40 to 50 years for the use of the power has been taken from this corporation by the Canadian company, and the Norwegian corporation already has more than 250 men at work.

*From The Journal of Industrial and Engineering Chemistry.

†Bureau of Animal Industry, Washington, D. C.

THE NITRATION OF TOLUENE.

The Nitration of Toluene, by E. J. Hoffman, has just been issued as Technical Paper 146, by the Bureau of Mines, Department of the Interior.

This paper is the result of experiments made in the explosives laboratory of the Bureau of Mines on the preparation of trinitrotoluene from toluene obtained in the manufacture of water gas. A brief outline of the theory of toluene nitration and a review of technical methods for the manufacture of trinitrotoluene are given. The experimental part includes a comparison of several different procedures for obtaining the desired product and the investigation of the effects of varying proportions and concentrations of nitrating acids and the influence of the temperature of nitration on the yield and quality of product. As a result of the experiments a method is outlined which the author believes will give the best results in the preparation of trinitrotoluene.

The method involves (a) the preparation of mononitrotoluene, and (b) the further nitration of the crude mononitrotoluene into trinitrotoluene. The acid used in the preparation of the mononitrotoluene is a mixture of two parts by weight of sulphuric acid (specific gravity 1.84) and one part of nitric acid (specific gravity 1.42), the weight of nitric acid taken being 50 per cent in excess of that required theoretically for the conversion of all the toluene into mononitrotoluene. The maximum temperature of nitration is 30° C.

The conversion of the crude mononitrotoluene into trinitrotoluene may be considered as performed in two stages, but without a separation of the dinitrotoluene formed in the first stage. The crude mononitrotoluene is dissolved in sulphuric acid (specific gravity 1.84), the weight of this acid being equal to the weight of mixed acid to be used in the first stage. The mixed acid consists of equal parts by weight of sulphuric acid (specific gravity 1.84) and nitric acid (specific gravity 1.5), the nitric acid content being 50 per cent in excess of that required theoretically to convert the calculated yield of mononitrotoluene into dinitrotoluene. The maximum temperature of nitration should not exceed 100° C.

At the conclusion of this stage in the nitration the acids in the nitration mixture are concentrated by the addition of 15 per cent oleum equal in weight to that of the mixed acids to be used in completing the nitration. The latter consists of equal weights of nitric acid (specific gravity 1.5) and 15 per cent oleum, the nitric acid being double that required theoretically to convert into trinitrotoluene the nitration products calculated as dinitrotoluene. The temperature of nitration must not exceed 117° C.

This method yielded a water-washed product of approximately 75 per cent of theory which melted at 78-80° C. and approximately 8.5 per cent melting below 75° (from the spent acid). Washed with alcohol-

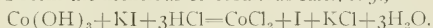
benzene mixture the yields were approximately 69 per cent melting at 79-81° C. and 7.5 per cent melting at 78-81° C.

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF COBALT.*

By W. D. ENGLE and R. G. GUSTAVSON.

As the quantitative determination of nickel and cobalt in the presence of one another is difficult, this investigation was undertaken to find, if possible, simpler methods than those commonly used. It was hoped that volumetric methods might be found whereby either of these metals might be easily determined in the presence of the other. A very satisfactory method for cobalt has been found, but in the case of nickel nothing better than the methods already in use has so far been discovered.

In the presence of sodium or potassium hydroxide both nickel and cobalt are oxidized to trivalent oxides or hydroxides by various oxidizing agents, but neither trivalent nickel nor cobalt forms stable salts with acids. Both nickelic and cobaltic hydroxides, when treated with acids and potassium iodide, liberate iodine and form the nickeloous or cobaltoous salts, *e. g.*,



Of these two metals, cobalt is the more easily oxidized, and when oxidized, forms the more stable compounds. For example, cobalt sulphate treated with potassium hydroxide and hydrogen peroxide gives cobaltic hydroxide, while nickel under the same treatment is not changed even at the boiling point. A. Metz¹ uses this fact as a basis for the determination of cobalt. The difficulty in completely removing the excess of hydrogen peroxide either by boiling or filtering and washing, is an objection to this method. After trial of a number of oxidizing agents, sodium perborate proved to be the best, both because it completely oxidizes the cobalt without affecting the nickel and also because any excess of the reagent is readily decomposed by boiling.

The method recommended is as follows: The ore, or other material, may be dissolved with acids and the metals of the copper and iron groups and also manganese removed by standard methods. The solution so obtained may contain nickel and cobalt, zinc, and the metals of the alkalis and the alkaline earths, but must be free from any substances capable of liberating iodine from an acid solution of potassium iodide. This solution, with a volume of about 100 cc., is made acid with dilute sulphuric acid, using about 5 cc. in excess, and 1 or 2 g. of dry sodium perborate added. After agitation and solution of the perborate, sodium hydroxide is added to strong alkaline reaction and the mixture boiled for 10 min. to decompose the excess of perborate. The solution is now cooled

*From the Journal of Industrial & Engineering Chemistry, Vol. anal. Chem., 33 (1914), 537.

to room temperature and, after 1 g. potassium iodide has been added, acidified with dilute sulphuric acid. After solution of the precipitate, the liberated iodine is titrated with a standard solution of sodium thiosulphate, using starch paste as an indicator.

As it is difficult to secure a cobalt compound of known cobalt content, it is recommended that the sodium thiosulphate solution be standardized by means of potassium dichromate in the usual manner. Since $1\text{K}_2\text{Cr}_2\text{O}_7=6\text{I}=6\text{Co}$, the $\text{K}_2\text{Cr}_2\text{O}_7$ factor of the thiosulphate solution multiplied by 1.2027 gives its cobalt factor.

If a cobalt compound of known purity is available, it may be used to standardize the sodium thiosulphate solution by taking a weighed quantity and treating, as in the regular method, with sodium perborate and sodium hydroxide. After boiling for 10 mins., cool, add potassium iodide and acidify with dilute sulphuric acid; titrate the free iodine with the thiosulphate solution and compute its factor. By this method 0.1613 g. of cobalt as cobalt sulphate required 35.23 cc. of the sodium thiosulphate solution, making its factor 0.004575 while its factor is determined by the potassium dichromate method was 0.004568.

The results of a few of the analyses of mixtures of cobalt and nickel are given in Table I. The cobalt used was a solution of pure cobalt sulphate containing 0.00078 g. of cobalt per cc. The nickel used was a solution of nickel sulphate free from cobalt and contained 0.00908 g. of nickel per cc. The titrations checked one another within a 0.1 cc. and wide variations in the amounts of the sulphuric acid, sodium perborate, etc., used did not affect the results. It may be noted that the process is accurate for widely different amounts of cobalt and also in the presence of large quantities of nickel.

TABLE I.—DETERMINATION OF COBALT IN THE PRESENCE OF NICKEL.

Expt. No.	Gram Nickel	Gram Cobalt—	
	Present.	Present.	Found.
1.....	0.0454	0.000	0.000
2.....	0.0908	0.000	0.000
3.....	0.0000	0.0489	0.0492
4.....	0.0000	0.0489	0.0487
5.....	0.0908	0.0489	0.0490
6.....	0.0454	0.0489	0.0491
7.....	0.4540	0.0489	0.0491
8.....	0.4540	0.0489	0.0495
9.....	0.0908	0.0978	0.0977
10.....	0.0908	0.0978	0.0982
11.....	0.0000	0.1467	0.1470
12.....	0.0908	0.1467	0.1466
13.....	0.0000	0.1956	0.1950
14.....	0.2270	0.1956	0.1955
15.....	0.0000	0.2445	0.2439

The following points in this analysis must be carefully observed to obtain accurate results: It is necessary to add the sodium perborate to the acid solution and then make alkaline. Attempts to add the perborate to the alkaline solution resulted in incomplete oxidation of the cobalt when the amount present was more than 0.050 g. It is necessary to add the potassium iodide before adding the dilute sulphuric acid for the solution of the cobaltic hydroxide, otherwise the results will be low. This method does not re-

quire the filtration of the cobaltic hydroxide, which is important not only in saving time, but in increasing the accuracy, as this compound tends to pass through the filter during the last part of the washing.

It was attempted to determine nickel and cobalt together by an analogous method using more powerful oxidizing agents such as bromine water and sodium persulphate. These experiments were not successful, due to the difficulty of completely removing the excess of the oxidizing agent. The nickelic and cobaltic hydroxides, which are readily formed, require filtration and excessive washing and even after prolonged washing the results were usually high. Cobalt free from nickel gave good results when oxidized with bromine water, but even here the washing required was excessive and the method is much inferior to the one given above using sodium perborate.

In conclusion we would state that cobalt may be determined in the presence of nickel by oxidation in alkaline solution with sodium perborate, removing the excess of the perborate by boiling, and after the addition of potassium iodide and dilute sulphuric acid, titrating with a standard sodium thiosulphate solution.

TO GET MELTING POINTS OF FATS.

A new process for the determination of the melting point of fats is described as follows in the *American Perfumer*. In the methods ordinarily in use the occurrence of melting is indicated by a fat layer of varying thickness. The thinner this layer, the more accurate the determination will be.

In the *Giornale di Farmacia e di Chimica*, No. 4, pages 151-153, the following process is recommended by Romolo Romarrelli: The apparatus consists of a wide-necked glass flask of about 250 ccm. capacity, into which a sensitive thermometer is introduced by means of a perforated cork. To the thermometer a platinum wire of a thickness of 0.3 to 0.4 mm. is attached, the free end of which is formed into a loop of a diameter of 8 to 9 mm. The wire is attached in such a manner that the loop assumes a vertical position, at an equal height, in front of the mercury ball. The flask is filled with unboiled, distilled water.

The fat to be examined is melted at a gentle heat. When it has cooled off almost to the solidification point, the platinum loop is dipped, parallel to the surface, into the liquid and quickly withdrawn. With a little practice a thin film of fat is obtained in the loop. This is allowed to cool for an hour, whereupon the platinum wire is attached to the thermometer in the manner stated and the flask carefully heated on an asbestos plate.

When the temperature approaches the melting point of the fat, the film of fat becomes transparent at the periphery. As soon as it is completely transparent, the layer breaks up and at this moment the melting point is read off, which in this manner can be very accurately and dependably determined.

PRICES OF CHEMICALS, OILS, ETC., OCTOBER, 1916

WHOLESALE PRICES PREVAILING IN NEW YORK MARKET ON OCTOBER 15

CHEMICALS, INORGANIC.

Acetate of lime, 100 lbs.....	\$ 3.50 @ 3.65
Alum, ammonia, crystals, lb.....	.04½ @
Aluminum sulphate, 100 lbs.....	.04 @ .05
Arsenic, white, lb.....	.06 @ .06¾
Barium chloride, ton.....	110.00 @ 115.00
Barium nitrate, kegs, lb.....	.14 @ .15
Bleaching powder, drums, 100 lbs.....	 @ 5.00
Blue vitriol, car lots, 100 lbs.....	12.00 @
Blue vitriol, powdered, 100 lbs.....	14.50 @ 15.00
Borax, car lots, f. o. b. N. Y., 100 lbs.....	7.50 @ 8.00
Brimstone, crude, ton.....	35.00 @
Caustic soda, 74 to 76%, lb.....	.03 @ .04
Chalk, precipitated, cases, lb.....	.06 @ .06½
Glauber's salt, bags, 100 lbs.....	.60 @ .64
Nitric acid, 36 to 42°, 100 lbs.....	7.50 @ 8.00
Phosphoric acid, 1.750 lb.....	.30 @ .34½
Potassium bichromate, lb.....	.39 @ .40
Potassium carbonate, calcined, 90 to 96%, lb.....	.80 @ .90
Potassium chlorate, crystals, lb.....	.53 @
Potassium cyanide, 94 to 96%, 100 lbs.....	1.00 @ 1.25
Quicksilver, flasks.....	80.00 @ 82.50
Silver nitrate, ounce.....	.42¾ @ .44¾
Soda ash, 48%, 100 lbs.....	2.12½ @ 2.25
Sodium acetate, lb.....	.11 @ .12
Sodium bicarbonate, American, 100 lbs.....	1.65 @ 2.00
Sodium bichromate, lb.....	.24 @ .25
Sodium chlorate, 100 lbs.....	.30 @ .35
Sodium hyposulphite, in bbls., 100 lbs.....	1.75 @ 2.00
Sodium nitrite, lb.....	.15 @ .18
Sodium sulphide, crystals, 100 lbs.....	2.50 @ 3.00
Sulphuric acid, 60° and up, cwt.....	1.50 @ 2.00
Sulphuric acid, 60°, ton.....	30.00 @ 35.00
Talc, domestic, spot, ton.....	15.40 @
Tin bichloride, 50°, 100 lbs.....	13.50 @
Tin oxide, lb.....	.44 @ .46

CHEMICALS, ORGANIC.

Acetanilid, lb.....	\$.55 @ .60
Acetic acid, 28%, 100 lbs.....	3.50 @ 3.65
Acetic acid, glacial, 99¾%, carboys, lb.....	.25 @ .30
Acetone, drums, lb.....	.22½ @ .23
Alcohol, denatured, 188 proof, gal.....	.57 @
Alcohol, grain, 188 proof, gal.....	2.68 @ 2.70
Alcohol, wood, 95%, gal.....	.70 @
Amyl acetate, gal.....	4.50 @ 5.00
Benzoic acid, from tululol, cwt.....	10.50 @ 11.50
Carbolic acid, drums, crystals, lb.....	.55 @ .58
Carbon, tetrachloride, lb.....	.16 @ .17
Chloroform, lb.....	.50 @ .55
Citric acid, domestic, crystals, lb.....	.67 @ .67½
Cresol, U. S. P., gal.....	.75 @ .80
Ether, U. S. P., 1900, lb.....	.15 @ .20
Formaldehyde, 40%, carboys, lb.....	.11½ @ .12
Glycerine, dynamite, lb.....	.45 @ .46
Pyrogallie acid, crystal, lb.....	2.90 @ 3.50
Salicylic acid, lbs.....	1.50 @
Tannic acid, technical, lb.....	.90 @ 1.00
Tartaric acid, crystals, U. S. P., lb.....	.66 @ .66½

DYE MATERIALS.

Acid orange, lb.....	\$ 1.75 @ 4.00
Aniline oil, drums, imported, lb.....	 @
Aniline, domestic, lb.....	.30 @ .35
Benzol (white), gal.....	.70 @ .75
Bismarck brown, lb.....	2.25 @ 2.85

Carmine, lb.....	4.50 @ 4.60
Cochineal, silver, lb.....	.65 @ .70
Cochineal, black, lb.....	.70 @ .75
Gambier, lb.....	.10 @
Indigo, madras, lb.....	1.07 @ 1.10
Logwood extract, 51°, lb.....	.22 @ .27
Madder, Dutch, lb.....	.21 @ .23
Methyl, violet, lb.....	6.00 @ 9.00
Methylene, technical, lb.....	10.00 @ 14.00
Prussian blue, soluble, lb.....	1.25 @ 1.30
Sulphur, black, lb.....	1.30 @ 1.90
Sulphur, brown, lb.....	.45 @ .50
Zinc dust, prime to heavy, lb.....	.25 @ .30
Zinc oxide, American, lb.....	.11 @ .12
Zinc sulphate, lb.....	.07½ @ .08

ESSENTIAL OILS.

Almonds, bitter, lb.....	\$ 12.50 @ 14.00
Amber, crude, lb.....	1.25 @ 1.50
Anise, technical, lb.....	1.00 @ 1.10
Camphor, Japanese, 72 lb. cans, lb.....	.16 @ .20
Cinnamon, lb.....	19.00 @ 20.00
Clove, lb.....	1.20 @ 1.25
Cubeb, lb.....	3.25 @
Ginger, lb.....	6.00 @ 6.50
Limes, distilled, lb.....	2.75 @ 3.00
Pennyroyal, prime, American, lb.....	1.65 @ 1.85
Peppermint, prime, American, lb.....	2.25 @ 2.40
Spearmint, oz.....	1.95 @ 2.10
Wintergreen, synthetic, oz.....	1.50 @ 1.60
Wormwood, oz.....	2.85 @ 3.00

FERTILIZER MATERIALS.

Ammonium sulphate, 100 lbs.....	\$ 4.00 @
Blood, dried, N. Y., 100 lbs.....	3.50 @
Bone black, sugar discard, ton.....	.27 @ .30
Bone, oil discard, ton.....	.18 @ .20
Phosphate, acid, per unit, ton.....	80.00 @ 90.00
Sulphate of potash, 90%, ton.....	 @
Tankage, Chicago, 100 lbs.....	3.30 @

OILS.

Castor oil, No. 3 bbls., lb.....	\$.13½ @
Corn oil, crude, 100 lbs.....	10.75 @ 11.00
Corn oil, refined, 100 lbs.....	11.51 @ 11.56
Cylinder oil, light filtered, gal.....	.26 @ .30
Cylinder oil, dark filtered, gal.....	.19 @ .20
Fusel oil, refined, gal.....	6.00 @ 6.25
Linseed oil, car lots, gal.....	.82 @
Menhaden oil, crude, Southern, gal.....	 @
Naphtha, auto, 68@72°, gal.....	.37½ @ .36½
Paraffine oil, high viscosity, gal.....	.29½ @ .30
Soya oil in bbls., lb.....	.10 @ .10½
Spindle oil, No. 1, gal.....	 @
Spindle oil, 20 gravity, gal.....	.17 @ .18
Tar oil, commercial, gal.....	.22 @ .23
Turpentine, gal.....	 @

WAXES, ETC.

Beeswax, ordinary, pure, lb.....	\$.32 @ .36
Ceresin wax, yellow, lb.....	.10 @ .30
Ceresin wax, white, lb.....	.14 @ .40
Japan wax, lb.....	.11 @ .14½
Paraffine, crude, 124-126 mp., lb.....	.05¾ @ .05¾
Pitch, pine, first grade, bbl.....	4.50 @
Rosin, B grade, N. Y., bbl.....	6.75 @
Stearic acid, lb.....	.11 @ .13½
Tar, retort, bbl.....	7.00 @ 7.50

NOTES OF CHEMICAL AND ALLIED INDUSTRIES.

Acid Phosphates.—The Standard Guano Co., 1500 Continental Bldg., Baltimore, Md., will erect a large acid phosphate plant at Curtis Bay, Md.

Air Production.—The Linde Air Products Co., 42d St. Bldg., New York, has awarded a contract to the Hettrick Construction Co., Dallas, Tex., to build plant at Birmingham, Ala., to manufacture oxygen for welding and other purposes. Electric power will be used and building will be of steel and concrete construction, to cost \$50,000.

Air Products.—Linde Air Products Co. is having plans prepared for a 1-story, 150x300-ft. factory to be erected at Chicago at a cost of about \$75,000. W. S. Barrett, 42nd St. Bldg., New York City, is in charge of construction.

Alkali Products.—The Brunner-Mond of Canada, Ltd., Toronto, Ont., has been incorporated recently with a capital stock of \$3,000,000 and is making preparations for the erection of a plant at Amherstburg, Ont., for the manufacture of alkali products. The Solvay Process Co., Syracuse, N. Y., is interested in the company.

Artificial Leather.—The Cincinnati Artificial Leather Co., Cincinnati, O., incorporated recently with \$15,000 capital stock, will fit up a plant on Wyoming Ave. for the manufacture of artificial leather. James Reid is president.

Barium Products.—The Stevens-Nixon Chemical Co., Geo. E. Nixon, secretary, 609 Mercantile Library Bldg., Cincinnati, O., will build plant at Covington, Ky., and install equipment to manufacture barium products, to include carbonate, chloride, chlorate, nitrate, sulphate, sulphide and sulphite; sodium sulphate, sulphide and sulphite; lithopone; also several by-products.

Benzol.—The Benzol Products Co., Marcus Hook, Pa., has awarded contract to F. W. Van Loon for the erection of a 2-story brick and steel factory building, to cost \$35,000.

Benzol.—Penn Mary Steel Co., Sparrows Point, Md., has awarded a contract to H. Koppers Co., First National Bank Bldg., Pittsburgh, for construction of 240 coke ovens and for benzol recovery plant for these 240 coke ovens and for the 120 now operating.

Cement.—The International Cement Co. will at once rebuild the two structures at its Irvine, Wash., plant that were destroyed recently by fire with a loss of \$100,000.

Cement.—The Oregon Portland Cement Co., Wilcox Bldg., Portland, Ore., proposes several improvements to its plant at Oswego, Ore. The plans include a river-front dock, conveying system, and a number of barges.

Cement.—The Three Forks Portland Cement Co., Lewiston, Mont., which recently took over the Hanover Gypsum Co.'s holdings and will construct a cement plant, has filed articles of incorporation with a capital stock of \$2,400,000.

Chemicals.—The Oconee Alkali & Chemical Co. of Athens, Ga., has been incorporated with a capital of \$100,000, by E. K. Hodgson, Jr., Harry Hodges, both of Athens, and J. S. Brogdon of Atlanta.

Chemicals.—The Marden, Orth & Hastings Co., Newark, N. J., manufacturer of chemicals, will build a 2-story brick ice-manufacturing plant and storehouse at Avenue R and the Plank Road, Newark, to cost about \$20,000.

Chemicals.—The Current River Furnace & Chemical Co., Kansas City, Mo., has been incorporated with a capital stock of \$50,000 and will equip a plant for the treatment and reduction of ores and the manufacture of chemicals. William A. Thompson, William A. Rule and W. H. Langford are incorporators.

Chemicals.—The Provident Chemical Works, S. H. Thompson, Treasurer, 8011 Idaho Ave., St. Louis, Mo., has awarded a contract for a \$200,000 addition to its St. Louis plant. C. H. Wray, 114 Rialto Bldg., St. Louis, is the architect.

Chemicals.—Roessler & Hassalacher Chemical Co., Perth Amboy, N. J., has secured an 80-acre site, 2 miles below St. Albans, W. Va., and will build \$1,000,000 plant to manufacture chemicals used in alloys.

Chemicals.—The Tennessee Chemical Co., Americus, Ga., has plans under consideration for doubling the capacity of its plant.

Chemicals, Paint.—The Southern Paint & Chemical Co., Birmingham, Ala., has been incorporated with a capital stock of \$40,000. L. K. Wiggins is President.

Cocaoat Oil.—Cocaoat Products Corp., 8 West 40th St., New York, proposes to build 317x118-ft. cocaoat-oil plant; 4-story mill and 1-story other buildings; fireproof construction; cost, \$140,000; West Construction Co., Knickerbocker Bldg., Baltimore, has the contract.

Cottonseed Oil.—The Wake County Cottonseed Oil Co., Raleigh, N. C., has been incorporated with a capital stock of \$50,000 by W. A. Simpkins, J. R. Chamberlain, and others.

Cottonseed Oil.—The Whitewright Oil Mill Co., Whitewright, Tex., has been incorporated with a capital stock of \$35,000 and proposes to build and operate a cottonseed oil mill. D. S. McMillan is interested.

Dyes.—The Holliday-Kemp Co., Woodside, N. Y., manufacturer of aniline dyes, has leased the Con-

sumers Brewery Bldg. at that place and will equip it for the manufacture of dyes.

Dyes.—The Central Dyestuff & Chemical Co., Newark, N. J., manufacturer of aniline dyes, has awarded a contract for additions to its plant on Plum Point Lane to be used as a pipe shop, carpenter shop and laboratory.

Glass.—The Dunkirk Glass Co., Dunkirk, N. Y., will double the capacity of its plant. Additions 80x200 ft., 2-story, and new furnaces will be erected.

Gypsum.—Foundation work has been started for the \$600,000 plant to be erected at Lewistown, Mont., for the Hanover Gypsum Co.

Limestone Products.—Basic Products Co. will build additions to double plant at Kenova, W. Va., and probably will invest \$250,000 for buildings and machinery. The company manufactures limestone products (dolomite, syndolad, etc.) for steel manufacturers.

Oil Refinery.—The Standard Oil Co. of New York has purchased 23 acres of land on Wawarme Ave., Hartford, Conn., and will erect two large plants, one a refinery, the other a distributing plant, which when completed will employ more than 2,000 workmen.

Oil Refinery.—The Texas Co., Houston, Tex., proposes to increase its capital stock from \$37,000,000 to \$44,400,000, the additional funds to be used to enlarge its oil-refining and marketing facilities.

Oil Refinery.—The Atlantic & Gulf Petroleum Co., Houston, Tex., which capitalized at \$1,500,000, contemplates building an oil refinery upon a tract of land which it owns, fronting the ship channel. R. E. Burt is president.

Oil Refinery.—The Security Producing & Refining Co., Irvine, Ky., will take out its incorporation papers in Delaware with capital stock of \$3,700,000 to develop oil lands in Estill County, Ky., build and operate refineries, etc. George B. Williams, Irvine, Ky., is president; W. Hume Logan, Louisville, Ky., vice-president, and John M. Hodkin, Winchester, Ky., secretary. The company has acquired rights on nearly 20,000 acres.

Oxygen.—The Bettendorf Oxygen-Hydrogen Co., Davenport, Ia., has increased its capital stock from \$50,000 to \$100,000.

Paper.—Philadelphia Paper Co., J. J. Jacobs, President, Nixon St., Philadelphia, Pa., has awarded the contract for a 1-story 150x50-ft. addition to its paper mill, to cost \$12,000.

Paper.—Chamber of Commerce of New Iberia, La., A. C. Bernard, Secretary, is interested in plan to organize company for manufacturing paper from bagasse, waste at sugar mills.

Paper.—The District of Columbia Paper Co., Washington, D. C., has placed orders for new building, machinery, etc., for a \$200,000 plant.

Paper.—The River Raisin Paper Co., G. H. Wood, General Manager, Monroe, Mich., has purchased 35 acres of land on the Shore Line Ry. at Monroe and will erect a paper plant in the spring.

Paper.—The Riverview Coated Paper Mill Co., Kalamazoo, Mich., proposes erection of a plant to cost \$500,000. The Kalamazoo Paper Co. also is planning to put up a new coating mill to cost about \$150,000. The two companies are composed of the same stockholders and have operated the two factories as separate parts of the same plant until recently.

Paper.—The Hought Paper Mills, Ltd., Camden East, Ont., has been incorporated with a capital stock of \$100,000. Lewis F. and Wilber E. Hought of Buffalo, N. Y.; Dan J. Albertson, Kalamazoo, Mich., are incorporators.

Paper.—The Riverside Paper & Fibre Co., Appleton, Wis., is expending about \$100,000 for electrifying its entire plant, enlarging the machine room capacity 100 per cent, and making other improvements and changes.

Paper.—Financial arrangements have been completed by George W. Whalen and eastern Canadian associates for the opening of pulp plants at Quatsino Sound and Swanson Bay, in addition to the present works of his company at Howe Sound, B. C. The Swanson Bay plant will have a daily capacity of 30 tons and Quatsino Sound 120 tons. The latter will be handled by the Colonial Pulp & Paper Mill, a corporation with a capital stock of \$2,500,000.

Paper.—Provincial Paper Mills Co., Ltd., will have plans prepared for a two-machine mill to be erected at Mille Roches, Ont.

Potash.—The Vermas Products Co., Santa Barbara, Cal., is constructing a large kelp reduction plant.

Potash.—Dr. R. S. Oppenheim and others are organizing the International Potash & Fertilizer Co. at Los Angeles, Cal., and propose to build a kelp reduction plant.

Potash.—The Hercules Power Co. has recently installed additional machinery at its kelp reduction plant at La Jolla, near San Diego, Cal.

Pulp.—The Fiber Co., Manistee, Mich., has been organized with \$300,000 and will begin work at once on a plant to manufacture pulp. The principal stockholder is E. G. Filer. Philip H. Schnorback, formerly of Muskegon, will be manager.

Pulp.—An agreement has been closed with the City Council, Port Arthur, Ont., whereby a company will establish a plant there for the manufacture of pulp, etc. It will have a capacity of 50 tons per day, which will be extended at a later date to 150 tons. Aimwell D. McIntyre, Toronto, Ont., is the promoter.

Pyrites.—The Pyrites Co., Ltd., South Wilmington, Del., will expend \$30,000 for improvements, to

include a 4-story chloriding building, 73x94 ft., of steel and concrete construction to cost \$20,000 and a precipitating tank, and two storage bins.

Silk.—Lewis, Riesel Co., 440 Fourth Ave., New York City, has awarded a contract to the Hogg Construction Co., Philadelphia, Pa., for the erection of an \$85,000 addition to its silk mill at Hazleton, Pa. William Binney is local manager.

Sugar.—The Wisconsin Sugar Co., Kurtis R. Froedter, President, Milwaukee, Wis., is preparing to resume operations in its big sugar mill at Menomonee Falls, Wis., and will add considerable new equipment, in addition to completely overhauling the present plant.

Sugar.—The required acreage has been signed up for the proposed sugar factory at North Yakima, Wash., to be established by the Utah-Idaho Sugar Co.

Tar.—The White Tar Co., Cliff & John Sts., New York, will build a refining plant on the Hackensack River, Kearney district, New Jersey, to cost about \$30,000.

Thymol.—North Tampa Land Co., Tampa, Fla., proposes erection of thymol distillery at Boyette, also erection of distilleries at North Tampa and Citrus Park.

Wood Alcohol.—The Barnum-Richardson Co., Lime Rock, Conn., has work under way at East Canaan, Conn., for the erection of a retort plant for the manufacture of wood alcohol and acetate of lime, with charcoal as a by-product. The charcoal will be used in the company's blast furnaces at East Canaan and Lime Rock. This is said to be the first plant of this type to be erected in New England.

Zinc Products.—The Canadian Zinc Products Co., Ltd., Montreal, Que., has been incorporated with a capital stock of \$45,000 to manufacture metals, zinc products, etc. Robert F. Macy, Portland, Me.; Leland D. Adams, Arthur R. Holden and others of Montreal, are incorporators.

SABADILLA IN THE WAR.

According to a press telegram from England recently published in Caracas the asphyxiating and tear-producing gases used in the present war are made from "Sabadilla," a product exported only from Venezuela, has caused considerable discussion in which the following facts have been brought out:

Sabadilla, known locally as "Cevadilla," a diminutive of the Spanish word Cebada, meaning barley, is the name of a plant of the lily family, botanically called "*Veratrum sabadilla* Retzrus," occurring only in Venezuela and Mexico. The highly-poisonous seeds have long been used in medicine. The substances produced from sabadilla seed are cavadine, or crystallized veratric, an alkaloid with the formula $C_{32}H_{40}O_9N$,

veratric acid ($C_9H_{10}O_4$), and Sabadalline ($C_{34}H_{53}O_8N$). This last is an amorphous, pleasant smelling alkaloid, that accelerates the beating of the heart.

While nothing is known here as to its use in the production of war gases, it is a fact that sabadilla dust irritates the eyes, the throat, and especially the nose so much that laborers working with it are obliged to wear protecting masks. Sabadilla powder is used by cattle raisers in this country as an insecticide with excellent results. It is stated that in Europe it is used in the manufacture of disinfectants, and that in the Balkan States and Russia it is employed in tanning fine leathers and as a mordant for dyes.

The first exportation from Venezuela was made to Hamburg 25 or 30 years ago. The foreign demand has never amounted to more than 5,000 sacks annually. Whenever production passes beyond this point the price has fallen below the cost of gathering. It is not a cultivated crop, but might become such if new uses were discovered which would cause an increased and regular demand. It grows in the vicinity of Caracas and is exported from La Guaira. The exports during the whole of 1913 and 1914 and the first six months of 1915 are given in Table I, the quantities given in kilos (1 kilo = 2.2 pounds), and the values in bolivars (1 bolivar = 19.3 cents):

TABLE I.

Country.	1913		1914		January-June, 1915	
	Kilos.	Bolivars.	Kilos.	Bolivars.	Kilos.	Bolivars.
United States			34,215	24,916	6,286	4,400
Germany	247,226	220,598	112,826	90,250		
France			2,300	1,840	13,435	9,405
Netherlands ..	9,320	7,992	16,400	11,479	65,687	45,468
Spain					840	588
Italy			3,487	2,440		
Total	256,546	228,590	169,228	130,925	86,248	59,861

For the entire year of 1915 exports of sabadilla to the United States, as declared at the La Guaira consulate and the Caracas agency, were 61,433 lbs., valued at \$9,097, as against 73,732 lbs., worth \$7,454, in 1914. The newspapers state that immediately after publication of the press telegram above mentioned the price of sabadilla in Caracas rose from 40 bolivars (\$7.72) to 60 bolivars (\$11.58) per 220 lbs., but that none is to be had in the market. The principal exporters are: H. L. Boulton & Co., Caracas (whose New York agents are Bliss, Dallett & Co., 82 Wall Street); Palenzona & Binda, Caracas; and E. Arenaga, La Guaira. [Sabadilla seeds and all preparations compounded from them have been declared contraband of war by England.]

Statistics just completed by the U. S. Geological Survey show that more natural gas was used in the United States in 1915 than in any other year. The quantity used was 628,578,842,000 cubic feet, which exceeds by nearly 37,000,000,000 cubic feet, or 6 per cent, the former record, established in 1914. Credit for the increased production of natural gas belongs to Ohio, Oklahoma, West Virginia, Pennsylvania, Kansas, and California.

Chemical Engineer and Manufacturer

Vol. XXIV.

NOVEMBER, 1916.

No. 5.

PUBLISHED MONTHLY by the MYRON C. CLARK
PUBLISHING CO.,

608 S. Dearborn Street, Chicago

*Entered as Second Class Matter, Aug. 19, 1907, at the Post Office
at Chicago, Illinois, under Act of March 3, 1879.*

Subscription—United States, Cuba and Mexico. \$2.00
Extra postage to Canada 25c a year; to foreign countries 50c a year.
Remittances may be made by check, draft or money order in favor of
CHEMICAL ENGINEER AND MANUFACTURER

All communications should be sent to CHEMICAL ENGINEER AND
MANUFACTURER, 608 S. Dearborn Street, Chicago, Ill.

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THE LABORATORY CONTROL OF A PLANT MANUFACTURING "C. P." BENZOL.

By ARTHUR C. NICOLET.*

The production of benzol of the purity required by the explosive and dyestuff industries requires continuous and rapid laboratory control. In one part of the operation results should be obtainable in 30 to 50 minutes and in some plants must be obtained within 1½ hours or 2 hours. If they are not obtainable within this time the operator has three courses open. He may stop that pure product still upon which results are not obtainable, which amounts to closing down that portion of the factory until results can be received. He may dump the unknown receiving drums into the pure product storage tank, which may contain as much as 15,000 or 20,000 gals. of the product, thereby risking the contamination of the whole. Or he may dump these drums into the "re-run" tank to be re-distilled later. The third course, obviously amounts to the same thing as the first.

For the purposes of this paper the reader will be assumed to understand the Koppers type of benzol recovery plant.

There are two points in the benzol plant where control is a necessity if the quality of final products is to be kept up. The remainder of the control work works for increased economy of operation and increased knowledge of how well the various steps are being carried out.

The two points where control is necessary are during and after the washing, with sulphuric acid and caustic soda, and after distillation from the pure product stills.

During and after washing two things must be tested for, thiophenes both during and after, and free acid after. Usually the product from the intermediate or fractionating still is given two or three acid washes, the spent acid being drawn off after each wash, before color test is made. The color test which is accomplished by shaking a sample of the oil being tested with one-half its volume of 50 per cent sulphuric acid, allowing to settle, and comparing the color of the acid with standards, shows whether further washing is necessary and indicates how much acid is required for the next wash. The result of not controlling this step would, of course, be the risk of

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†In this paper "benzol" will be considered as including the higher homologues, toluolxytol, and possibly some of the methylenes. For benzol alone "C. P. Benzol" will be used.

getting from the pure product stills a product which would not pass specifications and in addition a possible contamination of those stills which would require one or more profitless runs to eliminate. The danger in the other direction is the excessive use of acid with the consequent increase of expense and reduction of profits.

After the caustic wash, which is given only after an O. K. color test,[†] the only test made is for free acid. This test is accomplished by shaking a few cc. of the sample with an aqueous solution of some indicator, usually methyl orange. If this test shows a blank the oil is ready to run into the pure product stills for the final distillation. If it does not, another caustic wash is of course given. The harm done by free acid is not so much the harming of the final product, as the corrosion of stills, storage tanks and shipping drums. Once in a while the oil becomes contaminated with acid between the agitators and the still. In that event it is the practice in at least one plant to follow up the charge with several gallons of strong caustic.

The "control" of the pure product stills consists of analyses of a sample from each receiving-drum-full. Two things must be determined, the absence, or presence, of considerable quantities of the homologues of the substance produced (benzol xylols, etc., in the case of toluol and toluol xylols, etc., in the case of benzol) and the extent of thiophene contamination. The first of these is determined by the distillation of a measured volume, usually 100 cc. (customarily a 250 cc. ordinary distilling flask is used with the thermometer bulb at the outlet of the side tube) noting the "boiling point"—defined as the temperature at which the first drop distills over—the temperatures at which various defined volumes have distilled over, and the "dry point," which is the temperature at which the distilling flask becomes dry. In the case of "C. P." benzol the B. P. and dry-point are the only ones required. These, according to most specifications, should not differ by more than two degrees and should be near 80°. In the case of toluol two other points, the temperature at which 5 per cent has distilled over and the temperature at which 95 per cent has distilled over, are important. The second test applied to the supposedly "C. P." benzol and toluol is the same as that applied after the acid wash. The color developed should be slight.

The results of these tests decide whether the contents of the drum tested shall go into the pure product storage tank and thence to the buyer or to the re-run tank to be redistilled later.

Now we come to the strictly plant control analyses, or, better, tests. The most important of these is the "control" for the intermediate or fractionating stills. Here again the analysis consists of distilling a known volume of the sample and noting the B. P. dry-

point and the temperatures after the distillation of certain standard percentages. Here the intermediate points are of at least as great significance as either the boiling or dry points. These tests determine when the distillate flowing from the still shall be "cut" from the storage tank for one fraction into the storage tank of the next high boiling fraction, such as from "90 per cent benzol No. 1" to "90 per cent benzol No. 2," or from the latter to "90 per cent toluol." Some might call these tests necessary ones rather than advisable ones, but the writer prefers not to on the plea that the operator can from the speed and temperature of the distillation and other such indications near by enough to judge correct "cutting" point to permit the turning out of a satisfactory product from the pure product stills. He will, however, err sufficiently to increase somewhat the load on the pure product stills, decrease the proportion of pure product and increase that of re-run, thereby increasing production costs and decreasing profits. The extent of this damage should, however, be rather low with an experienced operator.

The rest of the tests are purely "control" and lacking any particular reason for any other order of consideration will be treated in the order of the sequence of the benzol through the plant.

The first of these is, obviously, the determination of the benzol in the gas as received. This is accomplished in a small experimental scrubber differing from the large scrubbers only in the number of units, in having artificial cooling and, possibly, in type of packing, and means of circulation (usually intermittent hand instead of continuous mechanical). These are loaded with benzol-free oil and a measured quantity of gas passed through at known temperature and pressure. The benzol in the oil is then determined, by distillation, and simple computations give the gallons per 1,000 ft. of gas or per ton of coal coked.

The next point of interest in the passage is the extent to which the large scrubbers have removed the benzol from the gas. This is determined in the same way as above. The relation of the two, of course, shows the efficiency of extraction.

The benzol in which the plant is immediately interested is now in the scrubber oil of the large scrubbers. Its determination is here, again, merely a matter of distillation. A larger quantity is, however, used here than in the case of the partially and completely purified products. A portion of this is distilled off and a second distillation made on this distillate. This test is run on the oil both before and after the primary stills in order to show how thoroughly they are doing their duty. Complete extraction is not expected but the more complete, of course, the greater the quantity of benzol in the oil as it meets the partially extracted gas and the less complete the extent of extraction.

The next test is the determination of the benzol in the distillate from the primary stills. The sample

[†]Some plants give a caustic wash preliminary to the acid wash in order to recover phenol. This preliminary wash does not, however, alter the sequence of the subsequent acid and caustic washes.

from this is usually taken direct from the storage tank and is of value in estimating the quantity of benzol recovered at this point and as an indication of the skill of the operator in avoiding "kickovers" of the stills with consequent increased contamination with extracting oils.

These tests complete the more important ones about the plant but besides them are the analysis of the crude naphthalene—secured through the chilling, settling and decantation of the residues of the secondary and pure product stills—the analysis of "solvent" as under American practice the higher homologues are usually bunched under the name of solvent naphtha, the spindling of acid bought for washing, and recovered from the washing and the caustic soda solution made up for the washing, periodic—usually daily or twice daily—analyses of the contents of the various storage tanks (these analyses serve as an insurance against mistakes being long undiscovered) and the testing of the scrubber oil purchased together with such other materials as may from time to time be purchased.

A NEW METHOD FOR THE DETERMINATION OF VANILLIN IN VANILLA EXTRACT.*

By ARTHUR W. DOX and G. P. PLAISANCE.†

The official method for the determination of vanillin in vanilla extract consists essentially in removing the alcohol, extracting the vanillin with ether, crystallizing it from the ethereal solution and weighing it directly, identifying the crystals if necessary by their melting point. This method was first proposed by Hess and Prescott.¹

Modifications were subsequently introduced by Winton and Silverman,² and by Winton and Bailey.³

For details of manipulation reference should be made to the official methods of the A.O.A.C.⁴

The whole operation is rather lengthy and tedious.

Methods dependent upon the precipitation of vanillin by various reagents have been suggested but have not come into common use. Hanus⁵ used m-nitrobenzoylhydrazide as a precipitant, and also platinum chloride⁶ for estimating vanillin in the presence of piperonal. Moulin⁷ converted the vanillin into a yellow methyl picrate and estimated it colorimetrically. More recently Folin and Denis⁸ have devised a colorimetric method based upon the color obtained by means of phosphotungstic and phosphomolybdic acids.

The writers⁹ have found that thiobarbituric acid in the presence of 12 per cent hydrochloric acid is a

general reagent for the precipitation of aromatic aldehydes and have applied it to the quantitative determination of furfural.¹⁰ Under these conditions vanillin gave with thiobarbituric acid an insoluble vermilion colored precipitate, which analysis showed to contain the percentages of nitrogen and sulphur required for the simple condensation product, 3-methoxy-4-hydroxybenzylmalonylthiourea. Since the reaction appeared to be practically quantitative, we decided to test out its possible application as a means of quantitatively estimating vanillin.

The first experiments were conducted with a standard solution of pure vanillin. Aliquots of this solution were precipitated with thiobarbituric acid in the presence of 12 per cent hydrochloric acid. The total volume of the reaction mixture was 50 c.c. The precipitates were allowed to stand over night, then filtered on Gooch crucibles, washed with 50 c.c. 12 per cent hydrochloric acid in small portions and finally with 20 c.c. of water. The results are set forth in the following table:

Vanillin taken g.	Wt. of precipitate g.	Vanillin recovered.	Error mg.
.0200	.0330	.0180	-2.0
.0200	.0337	.0184	-1.6
.0200	.0336	.0184	-1.6
.0200	.0330	.0180	-2.0
.0500	.0877	.0480	-2.0
.0500	.0890	.0487	-1.3
.0500	.0885	.0484	-1.6
.0500	.0890	.0487	-1.3
.0500	.0888	.0486	-1.4
.0500	.0906	.0495	-0.5
.0500	.0900	.0492	-0.8
.0500+	.0890	.0487	-1.3
.0500+	.0890	.0487	-1.3

+ Clarified with lead acetate.

In each case the filtrate was a lemon-yellow color, indicating that a small amount of the condensation product remained in solution. This observation is further substantiated by the fact that the vanillin recovered is somewhat less than the amount taken. The error is, however, quite uniform, regardless of the amount of vanillin taken, averaging 2.6 mg. of the condensation product or 1.4 mg. vanillin. It is apparent therefore that a solubility correction must be applied just as in the determination of furfural by the official phloroglucinol method.

Before applying the method to the determination of vanillin in commercial vanilla extracts, where clarification is necessary, the use of lead acetate as a clarifying agent was tested. In the last two determinations in the above table, lead acetate was added and the excess removed from the filtrate by hydrochloric acid before adding thiobarbituric acid. The results are in close agreement with the other results, showing that the small amount of lead chloride remaining in solution does not interfere with the determination.

A sample of vanilla extract of known purity was next used. The procedure was as follows:—25 c.c. of the extract were dealcoholized in the usual manner, then transferred to a 50 c.c. standard sugar flask and filled to the mark with lead acetate solution.

*From The American Journal of Pharmacy.

†Chemistry Section, Iowa Agricultural Experiment Station.

¹J. Am. Chem. Soc. 21, 256 and 719 (1899).

²Ibid 24, 1128 (1902).

³Ibid 27, 719 (1905).

⁴Bur. Chem. Bull. No. 152, p. 246.

⁵Zeitschr. Untes. Nahr. Genussm 10, 585 (1905).

⁶Ibid 10, 657 (1906).

⁷Bull. Soc. Chem. 29, 278 (1903).

⁸J. Ind. Eng. Chem. 1, 670 (1912).

⁹Dox and Plaisance, J. Am. Chem. Soc. 38, 2164 (1916).

¹⁰Dox and Plaisance, *ibid* 38, 2156 (1916).

After standing for several hours at about 37° C. the contents of the flask were filtered through a dry filter. The filtrate was a straw color, indicating the absence of caramel as added coloring matter. 40 c.c. of this filtrate was then transferred to another 50 c.c. flask. Sufficient concentrated hydrochloric acid was added to bring the volume to 50 c.c. and the acidity to 12 per cent. After standing a few minutes the lead chloride was removed by filtration through a dry filter and 40 c.c. of the filtrate taken for the determination. On adding thiobarbituric acid in 12 per cent hydrochloric acid solution, an orange colored precipitate resulted, indistinguishable in color from the product with pure vanillin. However, the color of the filtrate was somewhat darker than with vanillin alone, due no doubt to the original color of the filtrate after clarification. The precipitate was allowed to stand over night filtered on a Gooch crucible, washed with hydrochloric acid and water as in the previous determination and dried at 98°. The results were as follows:

Vanilla extract taken c.c.	Aliquot % of extract taken.	Wt. of precipitate g.	Wt. of precipitate corrected for solubility.	Vanillin found in aliquot.	Vanillin in 25 c.c. extract g.	Vanillin in extract per cent.
25	64	.0450	.0476	.0260	.0406	0.16
25	64	.0450	.0476	.0260	.0406	0.16
25	73	.0501	.0527	.0288	.0400	0.16
25	73	.0498	.0523	.0286	.0397	0.16
25	73	.0510	.0536	.0293	.0407	0.16
25	73	.0501	.0527	.0288	.0400	0.16
25	73	.0502	.0528	.0289	.0401	0.16
25+	80	.0896	.0916	.0501	.0626	0.25
25+	80	.0882	.0908	.0496	.0621	0.25

+Not clarified.

The above method is not applicable to artificial extracts where caramel is added as a coloring matter, since caramel contains furfural derivatives which react with thiobarbituric acid. The absence of caramel should first be demonstrated qualitatively. When caramel is present, the filtrate after clarification is brown instead of straw-colored. A still more delicate test, described here for the first time, is the reaction with phloroglucinol. After clarifying and removing the excess of lead as chloride, phloroglucinol is added. In the presence of caramel a brown precipitate is formed. If caramel is absent, the vanillin gives a delicate rose pink color or a slight pink precipitate. Clarification of the sample is necessary, as shown by the fact that the two determinations without clarification gave high results.

Thiobarbituric acid, which is easily prepared from malonic ester and thiourea, may be used for the quantitative determination of vanillin in vanilla extracts which do not contain caramel as added coloring matter. When caramel is present it may easily be detected by the brown precipitate formed on the addition of phloroglucinol to the clarified extract containing 12 per cent hydrochloric acid.

DEVELOPMENT OF OUR POTASH INDUSTRY.*

By F. M. deBEERS.†

American chemists have been looking for potash in this country for a great many years and several deposits and sources were discovered years ago and then neglected by capital, because of the moderate price of the German article. Most, if not all, of the present sources were known before the war, but the industry did not seem then to promise returns large enough to warrant the hazard of the new undertaking. Consequently nothing was done until our supply was suddenly cut off and a brief review here of what we bought on the average per year from Germany may not be out of place.

In round figures the following list shows approximately what we imported each year:

	Tons.
Potassium muriate (80 per cent).....	250,000
Potassium sulphate (90 per cent).....	50,000
Manure salts (20-38 per cent).....	200,000
Kainit (12-15 per cent).....	500,000
Total	1,000,000

Figuring all the potash as K_2O or potassium oxide would show about 360,000 tons of the oxide in the above importation. Our yearly supply of German potash cost us about \$20,000,000 before the war. During the balance of this paper when I refer to percentage of potash I will mean per cent of potassium oxide or K_2O .

The question of whether we can produce this large amount of potash here and take care of our increasing demand is entirely too large for me to even consider, particularly as no one seems to know when the war will end and what Germany plans to do then. We know she can produce potash very cheaply and we also know we have large but scattered supplies of potash-bearing materials here, but the whole thing is in too primitive a state now to warrant any guesses.

Some of our present developments will survive any competition, but others are simply intended to fill a present demand. In this paper I am only attempting to explain where we can secure our raw potash salts and what has been done up to the present that has come to my notice. The refining and purification of these raw salts has been done here before the war, and our large chemical companies can without doubt take care of this phase of the situation. Some of these raw salts can, of course, be used in their raw state in certain industries. Most of my information is first hand and my estimates as to quantities are of course approximations. I wish here to say that some of my information was obtained from reports by experts in other industries and to all these men I acknowledge my indebtedness.

*Paper presented at the 11th Annual Convention of the American Meat Packers' Association, Cincinnati, Oct. 9-11, 1916.

†President Swenson Evaporator Co., Chicago.

Our sources of supply can be divided into two classes, one containing those which are by-products and the other class consisting of industries where potash is the principal product. We will consider the by-product potash first.

Wood ashes have been the source of potash ever since our ancestors knew how to use same. After the German industry had developed the making of potash from ashes was practically abandoned, but lately I believe our supply is being augmented from this source. I have not been able, however, to locate any data that is sufficiently complete and reliable as to what we can expect in total tonnage, etc. I am of the opinion that this source is not of very great importance from a commercial standpoint.

Bittern produced in the manufacture of salt from sea water contains potash, but the quantity is very small and it is very difficult to separate from other salts. Bittern from the water of our Great Salt Lake is now being treated by three companies, and this runs about 2 per cent potash. Each company has its own method of separation and purification, and if they all operate up to their expected capacity they could turn out approximately 30,000 tons of raw salts per year, running about 20 per cent potash.

This figure is only approximate, as before stated, but it will serve to show that this source is not very important and high freight rates to Eastern points make it appear as if this process might have a hard time surviving after the war. The bittern also contains about 5 per cent magnesium oxide and, because of same, my conclusion may be unfair.

Wool is scoured or washed before it can be made into yarn, and this wash water contains about 3 per cent total solids after the wool grease and dirt have been separated out. These solids will average over 25 per cent in potash and are easily recovered. This material is available at the Atlantic Seaboard and, because of the value of the wool grease, it is very probable that the manufacture of potash in this way can be commercially successful. Another reason for saving this waste lies in the fact that by doing so this objectionable wash water is not run into streams or sewer systems. While the potash made should be easily marketable, the quantity obtainable from this source cannot be very great and I regret I have no figures as to tonnage. The potash is in the form of carbonate and potash soaps.

Fish water produced in menhaden factories contains about 8 per cent solids, and these solids will average 5 per cent K_2O and over 16 per cent ammonia. This cooking water should be saved and can be converted into a most profitable by-product. The industry is not a large one, however, and not more than 15,000 tons of dry fertilizer averaging as above could be produced per year based on the average kill of our Atlantic factories for the past five years.

In the making of alcohol from cane molasses there is a liquid residue left in the still which contains 5

per cent solids. These solids will average 9 to 10 per cent potash and also contain some ammonia. The potash is probably in the form of carbonate and sulphate. A few distilleries are now saving this slop and recovering the potash. If all the slop made in this way were saved and the solids recovered, we could count upon a production of about 200,000 tons of 10 per cent potash per year as a maximum, and I am inclined to believe that this estimate of mine is a little too high.

Many of our beet sugar factories employ the Stefens process for recovering the sugar from their molasses, and after the sugar is made in this way there remains a waste solution averaging about 4 per cent solids. Approximately half our factories have this waste material. These solids can be recovered and many European factories are doing so, but up to the present time our sugar makers, with a few exceptions, have done nothing. A dry product made from Stefens water will average over 6 per cent in ammonia and over 12 per cent in potash in the form of carbonate. Our American farmers will probably produce seven million tons of beets this year, and if the Stefens process were used in every factory and all the water were saved, we could count on about 200,000 tons of product per year of the above analysis. We are expecting a decided and permanent increase in our production from this source within the next year.

In the manufacture of cement, the dust leaving the furnace carries a considerable quantity of potash salts, and these are being recovered by several methods. The most successful seems to be the Cottrell system and very large returns are obtained according to several authorities. I have estimated roughly that we could produce about 80,000 tons of potash annually in this way if the figures given me are correct. It is sufficient to say that several plants are now using this process successfully and one plant is now being built near Buffalo that will turn out potash as the main product and cement as a by-product. This, of course, is a development of the feldspar situation to be discussed later.

Furnace gases from blast furnaces contain potash due to the volatilizing of the potash salts by the high temperature. This probably produces potassium cyanide and the amount of potash that passes away is enormous. My own figures seem so large that I am afraid of them, mainly because I have not had any direct experience or contact with this problem. If the statements of authorities, who have written in high-class journals are correct, this is one of our largest sources of potash and is, no doubt, being investigated thoroughly (and quietly) by the large producers of pig iron. The dust which settles in the stoves and boilers is now collected and sold to refiners of potash salts, although I could not find any data as to quantity.

The making of potash from kelp is being carried out with partial success on the Pacific Coast. The

present high value of this material and the absolute necessity of securing a supply has made it logical for some large users to put up plants for this purpose, and they are good investments no doubt for these reasons. I cannot see how this can be a permanent industry with potash at the price it was before the war unless someone perfects a process that will permit of a lower cost of production. This, of course, is only my private opinion, and I hope I am wrong, which is easily possible, as I have not had the opportunity to study the matter as closely as I would like to. If the kelp is thoroughly dried or burned, I am told it is possible to secure a product running over 15 per cent potash. So far as I know, no figures are obtainable as to production.

This about takes care of the development of our by-products as a source of potash. The remaining sources can be grouped under four headings: kelp, alunite, Western lake waters, and feldspar. There are some other minerals which contain potash, but personally I have not learned of any which are in sufficient quantity to be considered.

Potash from alunite is being successfully made in Utah, and I believe this industry is a permanent one. One of our large packers is responsible for the first commercial plant, and I am told that outside of the setbacks which must be expected in such a new development, the process is a success. According to my own figures, which are simply estimates, I would say that the production next year should be at least 20,000 tons of potassium sulphate 90 per cent pure—a very high-grade product. Other plants are now being contemplated, and we may soon have a much larger output. The ore itself runs from 8 to 12 per cent in potash and the process of manufacture is relatively simple.

The largest source available for quick use is out in western Nebraska and Wyoming. This field, to my way of thinking, is also a permanent one, and after the business has been standardized and the necessary experience secured, I believe our Nebraska friends can compete, if necessary, with Germany within a reasonable shipping radius. There are a large number of these small lakes running from a few acres up to several hundred acres apiece. Those containing potash salts have vegetation around their banks, while the alkali or soda lakes are barren. You will very often find two lakes side by side with potash in one and not in the other. Experts are now at work trying to locate the source of the potash that drained into these ponds and, if they are successful, we will probably be relieved of any worry as regards our supply. These lakes or ponds will average 10-16 per cent total solids and these solids when dried will contain 15 to 30 per cent potash, depending upon which lake is being worked. A fair average would be $12\frac{1}{2}$ per cent solids containing 20 per cent potash. One small lake alone which is being worked now is said to contain over 300,000 tons of these salts. A

large number of lakes have been bought and will be developed as soon as the new plants can be finished. This field should be permanent at least for a good many years before the lakes are drained. I should say that by the first of next January we will be getting 20 per cent potash salts from this district at the rate of 100,000 tons per year as a minimum.

Oregon has several lakes that contain very large quantities of potash as sulphates and carbonates. Some work is being done, but so far as I know there have not been any developments on a commercial scale up to the present time. I learned of one lake recently that I am told contains 18 per cent total solids of which 8 per cent is potassium carbonate, which certainly sounds very interesting.

Searles Lake in California contains a large quantity of potash, and a great deal of money has been and is being spent to produce a marketable product. The problem is not an easy one, as the brine contains a mixture of potassium and sodium sulphate, carbonates, chlorides and borates. They are very hard to separate, although I know that several hundred thousand dollars have been spent on a plant within the last year by the American Trona Corporation, which anticipates a large tonnage of potash salts soon. The brine used contains over 30 per cent total solids with about 5 per cent of potassium chloride. The company is figuring on an output of 40,000 tons per year of 80 per cent muriate, and so far as supply is concerned, they could operate at many times that rate for years to come, as the lake is very large.

Feldspar occurs in so many localities that we are all hoping that some American chemists will soon solve the problem of how to make potash from same on a commercial scale. The supply is practically unlimited. It averages from 8 to 15 per cent potash in the form of silicate and aluminate. One syndicate of miners in Colorado is producing 2,000 tons of finely ground and washed feldspar each day, which is all ready for a satisfactory process. Hundreds are experimenting, and if I had time I would be glad to explain some of the methods being tried. As soon as an economical method is discovered, we need have no fear about our supply, but such a method must be able to produce at a cost comparable with Germany's cost, which up to the present time has not been done to the best of my knowledge.

I have not attempted to explain any particular process used in making potash from any of these raw materials, as such information to be complete would result in a book, rather than a paper. After studying this question as carefully as possible, I am of the opinion that we will produce raw potash salts next year in sufficient quantity to supply about one-third of our average demand before the war, or equivalent to 120,000 tons figured as potassium oxide (K_2O). There is a chance that we may exceed this by 50 per cent if certain properties are worked or if new processes are developed, but even then we would have

but half our requirements during normal times, and right now we could really use more than that. Our future as a large producer depends entirely, to my way of thinking, on our success with feldspar, alunite, blast furnace gases, Searles Lake and other lakes in Nebraska, Wyoming and Oregon. We cannot secure much more than about 15 per cent of our requirements from the by-products first discussed, although many of these should be permanently profitable.

THE NEW GARBAGE REDUCTION PLANT FOR THE CITY OF NEW YORK.*

By GUSTAVE R. TUŠKA.†

The City of New York is now engaged on the construction of a new reduction plant for the final disposition of all the garbage collected in the boroughs of Manhattan, the Bronx and Brooklyn. The capacity of this plant will be over 2,000 tons of garbage per day. It will therefore be the largest plant of its kind in the world and its construction will be of further interest in view of the fact that every possible improvement in the handling of garbage will be installed in this plant so as to enable the disposition of the garbage to be done in a thoroughly sanitary manner.

The most important consideration in the design and construction of this plant has been that it shall be built and operated after the most sanitary methods and the matters of first cost and cost of operation have been secondary considerations.

This plant will be located on Lake Island in the town of Greenridge, Staten Island, at the junction of Little Fresh Kill and Great Fresh Kill, about a half a mile from Arthur Kill or Staten Island Sound. It is being constructed and will be operated on its completion by the Metropolitan By-Products Company.

DESCRIPTION OF PROCESS.

The process to be used in this plant is that known as the "Cobwell Process." There are already two plants in successful operation using this system, namely, that handling the garbage of the City of Los Angeles, Cal., and that of New Bedford, Mass. Both these plants have been in operation for some years in the course of which the success of the process has been absolutely demonstrated.

The method of reducing the garbage under the Cobwell system is as follows: The raw garbage is placed in a closed tank called the reducer and covers placed thereon and sealed airtight. This reducer is a cylindrical digester eight feet in diameter and four feet high. It is constructed with jacketed walls and jacketed bottom. Into these jackets the steam which is used in the reduction of the garbage is delivered. The design of these jackets makes it impossible, under proper operation, for the steam to enter the tank or come in contact with the garbage. In the interior

of this tank there is an agitating device operated by power from the exterior. When the proper charge of garbage has been placed in the reducer and the covers placed thereon, the tanks are sealed and the solvent is pumped into the reducer and steam admitted to the jacketed walls. The heat from the steam which is transmitted to the garbage through the walls of the reducer, causes the evaporation of the solvent and the water in the garbage.

Garbage is usually composed of over seventy per cent by weight of water. The steam heat vaporizes the solvent and the water from the garbage, and these mixed vapors are drawn off from the reducer to a condenser. The economy in this method of evaporation rests on the fact that water is vaporized at a lower temperature when evaporated with a solvent having a low boiling point than when evaporated without such solvent.

The mixed vapors of the solvent and the water while in the condenser are then condensed to a liquid state and the water and solvent together are conveyed to a closed tank. Owing to the solvent being of lighter specific gravity than the water, the solvent and the water are separated by gravity, the solvent rising to the top from where it is drawn back to the storage tanks, from which it is pumped back to the reducers and used over and over again. The condensed water, which has been largely diluted owing to the jet condensers used, is discharged into sewers or waterways.

When the garbage has been thoroughly dried by this method, the solvent is pumped into the reducer and dissolves the grease. The solvent with the grease is drawn off into a closed tank or evaporator where the same is heated by steam pipes where the steam is kept separated from the grease. The solvent therein is vaporized and carried to a condenser, where the same is again liquified and carried to the storage tanks to be used again.

After the grease has been extracted from the garbage in the reducer, it is further dried by means of the steam in the jacketed walls and is now in the form of degreased garbage tankage, which is used for fertilizer purposes after being ground and screened.

It will be seen from the above description of the process that if there are any leakages or vents in any of the tanks or piping where the solvent is handled, more or less of the solvent is lost and thereby a substantial additional expense is imposed upon the operation of the system. Furthermore, under this system, the garbage is at no time brought in contact with the atmosphere, from the time of its original entrance into the reducer until after over twelve hours of cooking, it is finally discharged therefrom as finished products, dried, sterile and practically odorless. These finished products are grease and the tankage above referred to.

It will be seen from the above description that the process is one of straight de-hydration and from the time that the material is at the boiling point no further

*Paper read Oct. 11 at Convention of American Society of Municipal Improvements.
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chemical action in the material takes place. No process of "digestion" occurs and therefore the odors and gases incidental to such a process are not created. Only the volume of gas contained in the raw material is driven out and only the essential oils of an extremely volatile nature are carried over in the current of steam and solvent vapor evolved. That little or no conversion takes place in the operation is shown by the fact that in the de-hydrated material obtained at the end of the operation, there exists practically the same amount of unconverted starchy bodies as existed in the garbage at the time of its entrance into the reducer. The water condensed contains all the gases evolved and has when fresh a slight odor of the mixed essential oils. Some traces of alcohol are detected in the effluent and a very small quantity of fixed oils is carried over. Any ammonia evolved, if it has escaped the acid in the garbage, is neutralized by acid carried over in the vapor. Whatever albuminoid ammonia exists in the effluent is carried over by mechanical entrainment as dust particles during the period of the steaming out of the solvent.

The effluent from the plants employing the Cobwell process consists of almost pure water, this water being the condensed moisture drawn from the reducer while the garbage is being treated and from which the solvent has been extracted as completely as possible.

An analysis of the undiluted effluent, being an average sample of a day's run at the New Bedford garbage plant is as follows:

	Per cent.
Acidity calculated as Acetic Acid.....	.05
Total Solids	.10
Oxide of Iron (included in solids).....	.053
Total Nitrogen as Ammonia	.0031
Albuminoid Ammonia	.00012
Fixed and Volatile Oils	.0059
Organic Solids	.033

The effluent, after being exposed to the action of sun and air for thirty days, gave no evidences of putridity but did have a slight vinegar-like odor. At the time of flowing from the separating tanks where the solvent is recovered from the condensed mixture of water and solvent, there was a slight sweetish acid odor, resulting apparently from the mixture of essential oils and petroleum. This effluent is cold and gives forth no steam or vapor and the odor can only be located by coming within two or three feet of the flowing water before the same has been diluted.

The total amount of such effluent can be reckoned on the basis of fourteen hundred pounds to each ton of garbage handled. On this basis, the New York plant will from two thousand tons of garbage, produce three hundred and forty thousand gallons of effluent of this concentration per day.

Calculating the total materials passing off in the effluent, we have

Total Solids	2,800 lbs.
Total Ammonia	86 lbs.*
Albuminoid Ammonia	3.6 lbs.*
Organic Solids	924 lbs.

*Included in total solids.

It must be understood that the above figures are based on the undiluted effluent or the actual water contents of the garbage condensed in surface condensers. In the New York City plant jet condensers will be used. In these the condensate and the condensing water are intimately mixed and the dilution is very large. About twenty parts of cooling water are necessary and the consequent dilution of one to twenty results in an effluent without any perceptible odor and an extremely low solid and ammonia content.

Effluent from an experimental jet condenser employing water from city mains and not sea water, as will be used in the New York plant, showed the following analysis:

	Per cent.	Parts per mil.
Total Solids	.01	100
Organic Solids	.0048	48.4
Mineral Residue	.0052	52.5
Total Ammonia	.00024	2.4
Albuminoid Ammonia	.00005	.5
Oxygen Requirement		22

It is impossible that an effluent of this concentration can have any undesirable effects when run into a large body of water. Rarely does the effluent from modern sewage disposal systems show so low an analysis of undesirable bodies.

The only other possible source of odor during the entire reducing operation would be from the odor contained in the air and gases mechanically included in the green garbage prior to its entrance into the reducer. These gases plus the air in the reducer itself at the time of filling, are driven out by the first rush of solvent vapor. Only one small vent is provided in the entire plant for the escape of these gases with any possible odor which they may carry. This vent is located on the storage tank for the solvent. The entire volume of such gases resulting from the handling of two thousand tons of garbage in twenty-four hours would be but fifty thousand cubic feet. At the plants now in operation, the only odor detected at this vent has been that of petroleum, which either destroys the possible vent gases or else masks them.

As regards any odor from the tankage: when this material is taken out of the reducer, it is in a dry condition and very warm and when it is first exposed to the atmosphere there is momentarily a slight odor of dried material best described as a smell of stale gingerbread, due to the essential oils rising from the material when hot. No gases are generated and this odor lasts only during the period of dumping and is not perceptible outside the building.

It will be seen that in the operation of garbage treatment by the process to be employed in this plant there is no period of gas generation and no large volumes of decomposition and combustion gases given off as in digestion and drying. There is therefore no necessity for condensing, washing, or trapping odors or gases.

DESCRIPTION OF THE PLANT.

The garbage will be delivered at the plant in barges, so constructed that all water drained from the garbage in transit will be collected in a special closed tank located at one end of the barge. On the arrival of the barge at the plant these tanks will be automatically emptied by attaching a steam connection thereto and by means of the steam pressure blowing the drained water to tanks on shore; the steam also acting so as to disinfect the tanks. While in transit the barges will be covered by specially treated waterproof canvas covers so attached as to prevent the discharge of any of the garbage from the barges.

A canvas apron will extend from the barge to the dock to prevent any of the garbage falling into the water during the unloading of the barge. This apron is so designed that it will automatically move with the barge when the same is moved along the bulkhead to bring the various portions of the load under the hoist.

The garbage will be unloaded from the barges by two steam operated hoists, equipped with grab buckets. These grab buckets will deliver the garbage to closed conveyors of the steel scraper type which will convey the material to the reducers, located in the main building.

This main building is 200 ft. by 330 ft. and about 30 ft. high and of one story. This building contains the reducers, 250 in number, with the necessary conveyors (all of which will be of closed type) for the raw garbage, and for the dried tankage, also the piping for steam and solvent and the transmission machinery. The capacity of each reducer unit is from 8 to 10 tons of raw garbage per 24 hours, depending on the steam pressure employed. In the New Bedford and Los Angeles plants the capacity obtained from one unit is 8 tons per 24 hours, with a steam pressure of 70 lbs. Here the steam pressure has been increased to 150 lbs., thereby raising the temperature for de-hydration from 320° F. to 360° F., thereby increasing the capacity of the reducer. An increase in the capacity has also been obtained through the change in solvent. In other plants using this process gasoline is employed but in this plant there will be used a special solvent, which is a kerosene distillate obtained by use of a vacuum still, which distillate will be made at the works. A further economy will be obtained by so designing the circulating system as to return condensed water at 360° F. to the boilers.

Heretofore only surface condensers have been employed in the plants using this process but after a considerable amount of experimental work with jet condensers, it has been proven that the latter are more satisfactory as well as more economical. It has therefore been decided to use the jet type of condenser in this plant.

The grease with the distillate is piped from the main building to the stills which are of the vacuum type and the distillate there taken from the grease, condensed and delivered to the solvent storage tanks

and the grease to other storage tanks. The "grease" building where this work is done is 100 ft. long by 100 ft. wide and 25 ft. high. The dried tankage is conveyed by belt conveyors from the main building to the grinding and screening building.

Pan mills and rotary screens are employed. From the screening building the tankage is conveyed to the storage building which is 100 ft. long by 100 ft. wide and 40 ft. high. The material is distributed throughout this building by screw conveyors. The tunnels will be built through this building containing belt conveyors to automatically convey the stored material to the loading vessel through swivel spouts.

The boiler house with an engine room extension will be 140 ft. long by 50 ft. wide and 65 ft. high. Water tube boilers with automatic underfeed stokers will be used with a productive capacity of 7,500 boiler horsepower.

The plant will also comprise a machinery building 30 ft. by 160 ft. by 25 ft., containing pumps of a capacity of 21,000 gals. per minute. Also boiler, blacksmith, machine and pattern shops and storeroom, etc.

The storage tanks will have a capacity of 400,000 gal. of solvent, and 14,000 bbls. of grease. There will also be constructed the necessary administration building, machanics' dormitory building, etc., etc.

The estimated cost of this plant when completed for a capacity of 2,000 tons of garbage per 24 hours is \$3,000,000, the main items of which are as follows:

Buildings	\$ 500,000
Boiler plant, including concrete stack	190,000
Reducer units, including condenser, still and auxiliary equipment, at \$7,000 each for 250	1,750,000
Piping	250,000
Conveyors	125,000

THE METHOD OF TESTING BISULPHITE LIQUOR.*

By A. CHRISTENSEN.

The methods employed for testing calcium bisulphite liquors in the sulphite mill of the Nekoosa-Edwards Paper Company do not differ essentially from the methods generally employed in sulphite mills. Instead of the customary tenth normal test solution of iodine, a more dilute solution is used, one of sixteenth normal strength. The following outline of procedure will, it is hoped, be of value for practical workers. In regard to the standard solutions of N/10 sulphuric acid and sodium Thiosulphate it is suggested that these be prepared or purchased especially for testing and standardizing purposes.

The acid is tested by titration with N/16 iodine solution and N/16 caustic soda solution, using a 2 cc. sample. Care must be taken to keep the sample of the acid, which is to be tested, in a closed bottle, otherwise there will be a loss of free acid. The 2 cc. of acid is diluted in a beaker with about 50 cc. of dis-

*A paper presented Sept. 29 at a meeting of the Technical Association of the Pulp and Paper Industry, New York.

tilled water, a few drops of starch solution added, and N/16 iodine solution immediately run in until a permanent blue color is obtained.

Another 2 cc. of the acid is diluted with the same amount of water, a few drops of phenolphthalein added and then titrated with the N/16 caustic soda solution until a faint pink color appears. For very accurate determinations the sample could be made up in the following way:

Take 20 cc. of the acid, pour into a 100 cc. measuring flask, and fill up to the mark with distilled water; 10 cc. of this solution corresponds to 2 cc. of the acid.

One cc. of N/16 iodine solution corresponds to .002 gram sulphurous acid (total) and 1 cc. of N/16 caustic soda solution corresponds to .002 gram sulphurous acid (free).

Suppose by titration with N/16 iodine solution 40 cc. are used, the per cent total SO_2 will be:

$$\frac{40 \text{ cc.} \times .002}{2} \times 100 = 4.00\%$$

or the per cent can be read direct from the burette by dividing the number of cc. iodine used by 10:

$$\frac{40 \text{ cc.}}{10} = 4.00\% \text{ total } \text{SO}_2$$

If by titration with caustic soda 25 cc. are required, the amount of free SO_2 in the acid will be:

$$\frac{25 \text{ cc.} \times .002}{2} \times 100 = 2.5\%$$

or, by dividing the number of cc. used by 10 =

$$\frac{25}{10} = 2.5\% \text{ free } \text{SO}_2$$

The amount of combined sulphurous acid will be the difference between the total and the free SO_2 in this case:

Per cent total SO_24.00%
Per cent free SO_22.50%
Per cent combined SO_21.50%

The advantages of using N/16 testing solutions are: A more accurate test can be made, as the solutions are considerably weaker than the N/10 solutions, and no calculations will be necessary, as the strength of the acid in per cent can be read direct from the burette.

The N/16 solutions are made up as follows:

IODINE SOLUTION.

Dissolve in a 1,000 cc. measuring flask 600 grams potassium iodide and 300 grams iodine crystals in about 500 cc. of distilled water, shake until all iodine is completely in solution and fill up to the 1,000 cc. mark.

Use 200 cc. of this solution to make 1,000 cc. N/16 iodine. The solution should be standardized against N/10 sodium thiosulphate, 40 cc. N/16 iodine corresponding to 25 cc. N/10 sodium thiosulphate.

CAUSTIC SODA (NaOH).

Dissolve in a 1,000 cc. measuring flask about 320

grams sodium hydroxide sticks (purified) and fill up to the mark with distilled water. Eight cc. of this solution are sufficient to make 1,000 cc. N/16 caustic soda.

Standardize against N/10 sulphuric acid, using phenolphthalein as indicator; 40 cc. N/16 caustic soda corresponds to 25 cc. N/10 sulphuric acid.

If an exceptionally accurate test is required, the solutions should be made N/160 by diluting 100 cc. of the N/16 solution to 1 liter. The number of cc. N/160 solution used, divided by 100, will give the strength of the acid in per cent.

To bring a weak solution up to the proper strength: Suppose, when standardizing N/16 caustic soda solution, 40 cc. were required to neutralize 25 cc. N/10 standard sulphuric acid; this shows that the solution is too weak; for every 42 cc. of solution made up, there are 2 cc. of excess water, or if the total amount of caustic soda solution is 1,000 cc., there are

$$\frac{1,000 \times 2}{42} = 48 \text{ cc. excess water}$$

In this case sufficient stock solution must be added to bring 48 cc. up to N/16 strength.

If for every 1,000 cc. N/16 caustic soda solution 8 cc. stock solution are required, 48 cc. of water will take:

$$\frac{4 \times 48}{1,000} = .4 \text{ cc. stock solution}$$

When correcting a weak solution, the strength of the stock solution must be known.

TO WEAKEN A STRONG SOLUTION.

Suppose the titration shows that only 38 cc. of the caustic soda solution were required to neutralize 25 cc. N/10 standard sulphuric acid, this means that the solution is too strong; for every 38 cc. of solution made up, there are sufficient chemicals to make 40 cc. N/16 solution.

If the amount of caustic soda solution made up is 1,000 cc., we must add

$$\frac{1,000 \times 2}{38} = 52 \text{ cc. of water}$$

to bring the solution up to the right strength.

These calculations can also be used for iodine or any other test solutions.

The following apparatus and chemicals are required when testing the sulphite acids:

N/10 or N/16 iodine solution.

N/100 or N/160 iodine solution.

N/10 or N/16 caustic soda solution.

N/10 sodium thiosulphate.

N/10 sulphuric acid.

One 50 cc. burette with glass stopcock for iodine test solution.

One 50 cc. burette with rubber tube and clamp for caustic soda test solution.

Six beakers or wide mouth Erlenmeyer flasks, capacity 250 cc.

Four pipettes, 2 cc.

Four pipettes, 10 cc.

Two volumetric flasks, 100 cc.

Support for two burettes.

Six glass-stoppered sample bottles, 250 cc.

Bottle for distilled water.

accustomed itself to such risks, and on the other hand the cost of the process is much lower when in place of the pure oleic acid cheaper fats are used.

The Varrentrapp reaction is not confined to oleic acid, rather all unsaturated fatty acids are converted, in alkali fusion, into saturated ones of lower carbon-number, and it may be said in such a manner that for each double formation two carbon atoms are split off

TESTING TABLE FOR SULPHITE ACID.

Table for N/10 Solution.

For mills where the use of N/10 Solutions is preferred, the per cent Total and Frte SO₂ can be read off directly from the following table when using 1 Cc. sample of the acid:

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
.0	0.32	0.64	0.96	1.28	1.60	1.92	2.24	2.56	2.88	3.20	3.52	3.84	4.16	4.48	4.81	5.12	5.44	5.76	6.08	6.40
.1	0.35	0.67	0.99	1.31	1.63	1.95	2.27	2.59	2.92	3.24	3.56	3.88	4.20	4.52	4.84	5.15	5.47	5.79	6.11	6.43
.2	0.38	0.70	1.03	1.35	1.67	1.99	2.31	2.63	2.95	3.27	3.59	3.91	4.23	4.55	4.87	5.18	5.50	5.82	6.14	6.46
.3	0.42	0.74	1.06	1.38	1.70	2.02	2.34	2.66	2.98	3.30	3.62	3.94	4.26	4.58	4.90	5.22	5.54	5.86	6.18	6.50
.4	0.45	0.77	1.09	1.41	1.73	2.05	2.37	2.69	3.01	3.33	3.65	3.97	4.29	4.61	4.93	5.25	5.57	5.89	6.21	6.53
.5	0.48	0.80	1.13	1.44	1.76	2.08	2.40	2.72	3.04	3.36	3.68	4.00	4.32	4.65	4.97	5.28	5.60	5.92	6.24	6.56
.6	0.51	0.83	1.16	1.47	1.79	2.11	2.43	2.76	3.08	3.40	3.72	4.04	4.36	4.68	5.00	5.31	5.63	5.95	6.27	6.59
.7	0.54	0.86	1.19	1.51	1.83	2.15	2.47	2.79	3.11	3.43	3.75	4.07	4.39	4.71	5.03	5.34	5.66	5.98	6.30	6.62
.8	0.58	0.90	1.22	1.54	1.86	2.18	2.50	2.82	3.14	3.46	3.78	4.10	4.42	4.74	5.06	5.38	5.70	6.02	6.34	6.66
.9	0.61	0.93	1.25	1.57	1.89	2.21	2.53	2.85	3.17	3.49	3.81	4.13	4.45	4.77	5.09	5.41	5.73	6.05	6.37	6.69

One 100 cc. dropping bottle for starch indicator. (Dissolve 5 grams soluble starch in 500 cc. distilled water.)

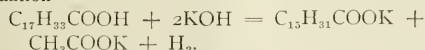
One 100 cc. dropping bottle for phenolphthalein indicator. (Dissolve 10 grams phenolphthalein in 1,000 cc. wood alcohol.)

IMPORTANCE OF THE VARRENTRAPP REACTION IN FATS AND SOAPS.*

By WALTER SCHRAUTH.

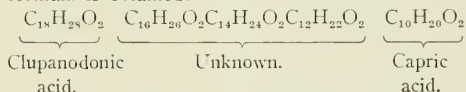
The conversion of unsaturated fats and fatty-acids into saturated is principally accomplished nowadays by direct hydrogenation in the presence of a catalyzer. All previous processes, without exception, have not proved satisfactory in practice. And yet it appears as though one or the other of these processes could be technically carried out with the now available means.

Especially does this apply to the Varrentrapp reaction, by means of which it is easily possible to convert oleic acid by melting with an excess of caustic alkalies into palmitic acid, in accordance with the equation



Here occurs, therefore, with simultaneous hydrogen development, a cleavage of two carbon atoms in the form of acetic acid, whereas the remaining carbon series is oxidized into palmitic acid. This process, which was technically carried out as far back as the seventies of the past century, has subsequently nowhere found adoption, on the one hand by reason of the risks entailed by the development of hydrogen occurring during the reaction; on the other, on account of the high cost that it entails. Both reasons no longer hold good, because, in the first place, the industry has

in the shape of acetic acid. For the clupanodonic acid (with four double bonds) as a result the following formula is obtained:



Now, clupanodonic acid, which is an important constituent of all train oils, is the cause of the characteristic train oil smell, which, with the progress of the destruction of this acid, must disappear. As a reaction product is finally obtained, a product that displays a certain resemblance to a coconut oil soap. Of course, by acidifying the fats, the fatty acids can also be recovered, which on distillation yield a snow-white distillate. The yield amounts usually to about 85 per cent of the fatty acids used (10 to 12 per cent loss through cleaving off of the acetic acids, 3 to 5 per cent through the distillation residue). The melting point of the resultant fatty acids lies between 35 and 40° C.; the iodine number is greatly reduced. The technical possibility of the process is admitted, especially if the process can be carried out with 50 per cent lye in place of the alkali flux. It is certainly necessary that the fatty acids are used because the glycerine in melting would be transformed into exceedingly offensive smelling acrolein.

As apparatus, it is best to use an autoclave of 5,000 liters' capacity, into which is placed about 2,500 kilos of train oil fatty acid, and 700 to 800 kilos of technical caustic soda, which has previously been dissolved in an equal quantity of water. Heat to 200° C., and raise in the course of about 6 hours to 260° C. The pressure must not exceed 10 atmospheres. The mass is then forced as hot fluid into a pan, and here either boiled directly into a marketable soap, or worked over for distilled fatty acids.

The addition of an oxidation medium, as prescribed by Riepel in his patent application, can be dispensed

*Translation from Deutsche Parfumerie Ztg., 1916, in The American Perfumer.

with the effect of the alkaline flux being in itself oxidizing. The technical effect following the adoption of the Varrentrapp reaction would consist, in the first place, in a saving of cocoanut and palm nut oil. Hydrogenized train oils are tallow-like, and can only be worked into lathering soaps by the addition of other fats and fatty acids, whereas, according to the process in question, fatty acids are produced, which, in their composition, display a certain resemblance to the vegetable fats. Of course the hydrogen formed during the Varrentrapp reaction can at the same time be used for hydrogenation purposes, and it is thus possible, from the same raw material, the fluid evil-smelling train oil to find, on the one hand, a substitute for tallow; on the other one for the vegetable fat.

A CENSUS OF THE ARTIFICIAL DYE-STUFFS USED IN THE UNITED STATES.*

By THOMAS H. NORTON.

The necessity for a complete enumeration of the artificial coloring matters, regularly consumed by the various manufacturing industries of this country soon became evident when these branches were threatened in 1914 by a dyestuff famine, as a result of the great European war.

Those who took into careful consideration the possibility of creating an independent American coal-tar dyestuff industry were obliged to study closely a number of factors bearing upon this exceedingly complicated question. Among these were such items as the supply of crude materials, the chemists and chemical engineers available, the probable attitude of the European interests, hitherto furnishing our synthetic dyes, upon the return of normal international conditions, the requisite fiscal and other legislation essential to safeguard American enterprise and capital against unfair competition on the part of such foreign rivals, etc.

First and foremost, however, came the factor of *quantity*. What is the total annual consumption of artificial colors in the United States? How many different dyes are in current use? What is the average annual consumption of each of these dyes?

The necessity of exact information on these three points is self-evident to some. For most, a brief explanation may be helpful.

In a general way we know how the great dyestuff industries of Germany and Switzerland are organized. We understand the relations of capital, of technical staff, etc., to output. From an economic standpoint it is necessary to know the total extent of the American market for this class of products, in order to estimate approximately the amount of capital required for a comprehensive industry, the number of trained chemists and engineers needed, and the quantities of coal-

tar trades to be provided. These form the main links in the chain connecting the gas works and the coke plant yielding coal tar and the gases laden with benzene and its homologues, with the multitude of mills and shops in which synthetic colors are employed to produce chromatic effects upon wares of the most varied nature—paper, textiles, leather, wood, ink, varnish, fur, feathers, foods, beverages, etc.

While such leading data are of prime importance from a general economic standpoint, of still greater value are the details concerning the specific products of the synthetic color industry.

NECESSITY OF A CENSUS OF DYES.

There are nearly 1,000 coal-tar dyestuffs of recognized standing in the tinctorial world; i. e., their chemical composition, or at least the methods of preparation, are publicly known. About twice as many are regularly manufactured, and enter into international trade, regarding the preparation or the composition of which little or nothing has been published. Many colors of both categories are encountered commercially in the form of several marks or brands. These represent slight modifications of the primary dye, sometimes in regard to shade, often in regard to convenience of application. The form in which a dye is prepared for use on cotton may not be the best form for the needs of the silk dyer. The requirements of the feather dyer may be quite different from those of the manufacturer of ink.

It is essential that the organizers of a national color industry know, with a certain approximation to accuracy, how much annually is consumed of each primary dye, and how much of each minor modification is employed. Without such data a manufacturer cannot calculate the size and number of the units to be constructed for the production of any given dye, and he is at an equal loss as to the equipment necessary to manufacture it in the different modifications of current use.

Again, the industry is one of great complexity, involving a high degree of co-ordination and of careful planning to avoid material loss in the way of by-products. In the various steps intervening between a coal-tar "crude" and a finished dyestuff, each chemical reaction in the sequence is apt to produce certain percentages of closely allied compounds, isomeric substances as a rule. These latter may possess the same general chemical composition as the product more directly sought. The arrangement of the atoms in the molecule is, however, quite different. As a result, physical and chemical properties are totally unlike those characterizing the main substances. Such by-products possess, as a rule, distinct technical and commercial value. One may serve to make an entirely different dyestuff, another may be the raw material for manufacturing a valued medicinal; a third may be employed in the production of a photographic developer, etc.

It is evident, therefore, that the establishment of a

*From the Journal of Industrial and Engineering Chemistry. Address delivered before the American Chemical Society, at the New York Meeting, during the Symposium on "American Dyestuff Manufacture."

synthetic color industry means an elaborate study of a multitude of inter-related operations, allied furthermore with numerous products in a group of closely connected industries, based likewise upon the use of coal-tar crudes. To some extent the changing whims of fashion enter into play. Back of every plan and calculation stands, however, the dominant factor of quality.

It is now generally recognized that any intelligent effort to build up a comprehensive, self-contained, American coal-tar chemical industry must rest upon the solid foundations of accurate statistical data concerning the American market for artificial colors. In no other way can the creators of such an industry avoid duplication, overlapping, waste, and blundering, tentative struggles to adjust productive mechanism to a vague, indefinite demand. Without such fundamental data the future industry will be heavily handicapped by permanent overhead charges, accumulated as the result of being forced to feel its way in the dark, chemically, mechanically, and commercially.

If the coming American dyestuff industry is to hold its own successfully against foreign competition, it must be free from any unnecessary shackle. It must start into existence during these years of crimson-splashed struggle for Europe—a golden opportunity for this republic—at the point where a brusque order to halt has been given the giant factories on the Rhine, the Main and the Spree. It must utilize to the full all the gathered stores of experience accumulated during the six decades since Perkin's epochal discovery, and become a world factor in the seventh period of the history of synthetic color, at whose portal we now stand.

To no one is this country more indebted than to Dr. Bernhard C. Hesse, of New York, for a clear, forcible presentation of the complexity of the synthetic dyestuff industry and of the pressing necessity of accurate data on the domestic consumption of artificial colors. Attention should be directed to his briefer studies on the subject in the *Journal of Industrial and Engineering Chemistry*, and to his more exhaustive paper before the National Association of Cotton Manufacturers, in April, 1915, and published in the *Textile Manufacturers' Journal*, May 1, 1915, p. 60.

ACTION OF THE BUREAU OF FOREIGN AND DOMESTIC COMMERCE.

Early in 1915 the embargo came into force, shutting off German dyes from this country. Long before, the relatively small supply of colors from England, France, Belgium and Holland had practically ceased and the somewhat more important source in Switzerland was threatened with paralysis.

The Bureau of Foreign and Domestic Commerce in Washington was following with the keenest interest, and even with anxiety, the initial steps taken bravely and resolutely by a small band of far-sighted American men, some manufacturers, some capitalists—all patriots—convinced that finally the opportunity had

arrived to build up a genuinely national coal-tar chemical industry.

In the earnest desire to second their efforts and facilitate their plans, as well as to insure the most favorable and economical conditions for the rapid evolution of the new industry on a permanent basis, it was promptly recognized, in harmony with the reasoning detailed above, that nothing could be of such direct assistance as a "census" of the dyestuffs consumed normally in this country. Plans were carefully laid to carry out the work as expeditiously, accurately, and fully as the very limited appropriations at the command of the Bureau for such general purposes would permit.

HOW THE CENSUS WAS TAKEN.

First of all it was necessary to decide upon the *modus operandi*. It was suggested by some, who had early recognized the desirability of such a "census," that the only available method for securing the needed data was to appeal to all consumers of artificial colors for their co-operation. It was thought that a ready response would be given to circular requests for detailed information regarding the annual consumption of coal-tar dyes by each user of the same. It was proposed, in order to overcome the customary repugnance of manufacturers to communicate facts of this nature, that the replies should be sent to some central financial institution, which would guarantee secrecy in collating the numerical information thus gathered.

A careful analysis of the problem showed that any such method of collecting data was impracticable. It would be impossible to secure a complete list of all users of dyestuffs in scores of trades and manufacturing branches. Assuming that figures could be obtained from all users of colors, their compilation would be a herculean task. Suppose that 5 tons of Congo Red are consumed annually in this country. This amount might be divided up among several thousand consumers, in lots ranging from 5 to 100 pounds.

With a somewhat elementary knowledge of human psychology, it was furthermore certain that no replies could be expected from the great majority of the recipients of circular requests. Indifference, suspicion, or pure laziness are serious factors to overcome.

BRITISH ATTEMPT TO TAKE A CENSUS OF COLORS.

The correctness of this conclusion has recently been abundantly verified by trans-Atlantic experience. British textile and allied interests have been forced to deal with a far more serious "dyestuff famine" than has been the case in the United States. There was a similar determination to build up a genuinely national color industry. The necessity of a dyestuff "census" was likewise recognized as of paramount importance. An influential committee, representing makers and consumers of dyes, took the matter in hand. Appreciating the futility of dealing directly with the multitude of individual users of colors, the committee decided to collect its statistics through the various powerful organizations of trades employing large quanti-

ties of dyestuffs and then double the results, thus roughly approximating at the entire national consumption of the various colors. After months of labor the committee was forced, in November, 1915, to report a practical fiasco. Replies were secured from but 19 associations or large individual consumers. The figures obtained covered but 3,145 short tons, perhaps 12 per cent of the national consumption.

FEATURES AND VALUE OF THE CENSUS.

The method adopted by the Bureau of Foreign and

Domestic Commerce was much more simple, direct and accurate. As in the case of Great Britain, nearly nine-tenths of the normal American consumption is derived from European sources. It was decided to use the data based upon the imports of artificial colors into this country during the 12 months ending June 30, 1914—a month before the outbreak of the present war. The remaining tenth is covered by the returns of the Bureau of the Census for the domestic coal-tar dyestuff industry based upon the production

SUMMARY OF THE MOST IMPORTANT COLORS IMPORTED BY U. S. DURING FISCAL YEAR 1913-14.

The abbreviation V.M. denotes "various marks." The serial numbers employed correspond to those found in Schultz's "Farbstofftabellen" (edition of 1914). Numbers preceded by letters refer to colors regarding the manufacture and chemical composition of which little or nothing is known. Azo dyes in this category are indicated by A, sulphur colors by S and other dyestuffs of unknown composition by U.

Serial No.	Commercial Name.	Lbs.	Invoice Value.	Serial No.	Commercial Name.	Lbs.	Invoice Value.	Serial No.	Commercial Name.	Lbs.	Invoice Value.
Class (10,000 to 100,000 lbs.)				Class (10,000 to 100,000 lbs.)				Class (10,000 to 100,000 lbs.)			
1	Nitroso and Nitro Colors.			212a	Acid Black (V.M.)	14,765	3,238	A 16	Columbia Fast Blue (V.M.)	84,661	18,879
4	Naphthol Green	19,146	\$2,902	217a	Acid Black (V.M.)	13,465	2,359	A 28	Naphthogene Blue (V.M.)	33,847	6,824
Sulbene Colors.				217c	Naphthol Blue Black (V.M.)	62,864	8,864	A 32	Nerol (V.M.)	65,441	9,751
9	Direct Yellow	71,399	11,295	217e	Acid Black (V.M.)	17,489	5,747	A 41	Colamine Blue B.	21,704	8,376
9a	Naphthamine Yellow (V.M.)	42,180	6,748	217g	Wood Black (V.M.)	23,371	7,438	A 69	Corvan Black (V.M.)	10,033	4,066
9b	Direct Yellow (V.M.)	19,055	16,784	217h	Acid Wool Black	13,518	4,202	A 71	Cotton Black (V.M.)	24,505	4,843
9g	Direct Yellow B.	29,192	2,765	220a	Amido Acid Black	32,624	3,614	A 81	Lithol Fast Orange R	36,641	4,381
10	Sulbene Yellow	50,477	7,464	236	Wood Red	13,245	1,942	A 88	Oxamine Black (V.M.)	50,032	10,472
10a	Sulbene Yellow RX	34,588	6,305	257	Toly Blue	16,750	2,967	A 95	Oxamine	93,454	22,569
11	Chloramine Orange	24,688	5,914	265	Sulfon Cyanine Black	69,590	7,663	A102	Oxamine Copper Blue R	10,222	1,941
12a	Diphenyl Orange	35,644	5,933	269	Acid Black	35,662	5,765	A104	Oxamine Dark (V.M.)	23,810	4,246
14	Diphenyl Chrysoine	9,898	3,071	272b	Wool Black (V.M.)	15,756	3,596	A108	Oxamine Dark Brown G. R.	10,599	1,312
18	Diphenyl Fast Yellow	9,656	2,988	275a	Chrome Black (V.M.)	72,521	13,616	A122	Palatine Chrome Blue BP	42,244	4,679
Pyrazole Colors.				275c	Chrome Fast Black	35,999	10,532	A124	Palatine Chrome Green	19,665	6,452
19	Fast Light Yellow	33,514	10,272	277	Anthracene Acid Black	17,793	2,847	A131	Scarlet (V.M.)	50,778	7,281
20	Flavazine S.	19,000	4,927	279	Benzo Fast Scarlet	36,674	9,010	A142	Wool Scarlet (V.M.)	32,780	1,417
20a	Flavazine (V.M.)	62,375	10,700	283	Bismarck Brown	27,576	5,352	A144	Acid Black E. M.	18,660	2,031
22	Xylene Yellow	23,074	9,750	288	Palatine Chrome Black	18,955	1,607	A147	Acid Chrome Black (V.M.)	39,508	8,052
Azo Colors.				296	Cotton Yellow	21,437	6,161	A150	Acid Sulf. Blue R	12,928	2,234
33	Chrysoidine	63,303	8,585	307	Renol Brilliant Yellow	12,786	3,290	A157	Benzo Chrome Black Blue B.	51,315	9,504
37	Chroceine Orange	11,366	1,535	307	Congo	12,040	1,687	A166	Benzo Dark Green B. GG	13,038	2,123
38	Orange G.	48,456	7,159	308	Digo Black	62,854	8,257	A176	Benzo Fast Heliotrope (V.M.)	13,018	5,541
45	Brilliant Lake Red R.	31,674	2,337	312	Congo Corinth	98,748	6,030	A184	Benzo Green (V.M.)	16,506	2,850
46	Autol Red	49,447	5,375	313	Congo Robin	46,113	6,329	A191	Benzo Red 10 B, 12 B	19,420	4,715
55	Mordant Yellow	26,870	4,112	319	Diamine Scarlet	28,887	9,027	A203	Benzo Rhoduline Red B. B.	11,873	1,813
58a	Alizarin Yellow (V.M.)	59,000	7,676	329	Oxy Diamine Violet	11,514	1,938	A210	Brilliant Fast Blue (V.M.)	11,553	3,309
58	Orange 13, 14.	10,974	2,634	332d	Diamine Violet N.	13,107	2,840	A215	Cashmere Black 3	12,269	1,881
61	Victoria Violet	47,126	10,298	333d	Develop Black	17,495	4,330	A227	Diaz Brilliant Scarlet (V.M.)	38,909	14,210
63	Azo Acid Blue	41,258	8,544	334	Diphenyl Blue Black	26,240	4,415	A242	Diaz Fast Black (V.M.)	29,220	7,476
64	Luafuchsine	68,055	9,375	338	Digo Black	62,854	8,257	A259	Direct Black (V.M.)	12,048	2,019
66a	Amido Naphthol Red	36,060	25,570	342	Diamine Fast Red	47,724	17,131	A266	Helio Bordeaux BL.	14,703	793
70	Brilliant Orange O.	21,483	8,835	344	Diamine Brown	63,716	12,457	A277	Orange RO	24,288	2,246
73	Helio Fast Red	13,413	2,441	348	Oxamine Red	63,716	12,457	A285	Phenylamine Black B.	14,066	1,619
73a	Lithol Fast Scarlet	36,295	9,287	348	Diphenyl Brown BN.	13,471	4,015	A286	Pluto Black (V.M.)	30,010	6,034
80a	Wool Scarlet (V.M.)	39,888	6,292	360	Pyramine Orange R.	21,329	7,818	A292	Pluto Brown (V.M.)	14,580	2,542
82a	Ponceau (V.M.)	20,972	1,931	365	Oxidine Orange	19,905	4,442	A303	Alphanol Black (V.M.)	30,159	3,124
88a	Acid Anthracene Brown (V.M.)	30,555	7,932	366	Benzo purpurine 5 B.	20,090	1,442	A336	Azo Wool Violet (V.M.)	12,944	3,298
96a	Chrome Fast Yellow	15,165	3,056	367	Deltapurpurine 5 B.	20,284	1,442	A346	Diamine Catechine	66,876	14,942
102	Diamond Flavine G.	23,080	4,226	370	Brilliant Congo	19,133	3,133	A351	Diamine Fast Blue (V.M.)	28,880	7,227
112	Bordeaux B.	10,174	1,474	381a	Diamine Blue (V.M.)	21,725	3,687	A355	Diamine Fast Orange (V.M.)	17,387	4,819
112a	Claret Red	14,338	1,291	392	Tolylene Orange	55,662	13,236	A361	Diamine Jet Black (V.M.)	14,091	4,315
118	Geranine	18,917	6,090	400	Acid Anthracene Red	17,560	5,174	A362	Diamine Neron BB.	26,982	6,204
126a	Union Blue (V.M.)	15,353	2,116	405	Benzo purpurine 10 B.	47,708	11,181	A367	Diamine Orange (V.M.)	17,068	2,851
132	Lake Red	40,345	2,019	410	Benzoazurine (V.M.)	78,639	21,018	A368	Diamine Sky Blue FF	41,115	7,574
137	Acid Yellow	35,882	6,313	416	Oxillium Azurine 5 G.	18,395	3,206	A384	Oxy Diamine Brown (V.M.)	23,498	3,810
139	Orange IV	11,238	1,966	420	Acid Anthracene Red	17,560	5,174	A385	Oxy Diamine Carbon (V.M.)	34,388	7,564
140	Carumine	39,269	6,257	425	Benzo purpurine 10 B.	47,708	11,181	A388	Para Diamine Black (V.M.)	18,634	2,690
141	Azo Yellow	59,894	13,755	429	Benzoazurine (V.M.)	78,639	21,018	A403	Sulfine Blue B.	16,224	8,449
141a	Azo Flavine (V.M.)	20,114	3,151	430	Benzo Fast Blue	73,936	20,607	A414	Amido Naphthol Black 4 B. RK.	10,750	1,219
141b	Indian Yellow (V.M.)	10,537	2,392	438	Diamine Brilliant Blue G	11,592	2,496	A418	Azo Acid Black (V.M.)	19,500	3,042
146	Azo Fuchsine G.	17,819	2,585	439	Chicazo Blue R. W.	15,476	3,364	A430	Fast Mordant Blue R.	17,000	4,612
147	Azo Fuchsine B.	13,206	1,867	440	Oxidine Green (V.M.)	19,313	4,291	A437	Naphthalene Blue B. DL	28,000	5,102
151a	Orange B.	90,174	7,394	441a	Oxamine Blue (V.M.)	21,800	3,749	A439	Victoria Scarlet R.	22,400	2,379
152	Permanent Red B.	44,850	14,513	426	Benzenamine Purc Blue	12,881	5,663	A444	Direct Green (V.M.)	31,194	5,091
152a	Permanent Red (V.M.)	56,545	7,403	429a	Direct Blue (V.M.)	21,322	5,366				
154	Palatine Chrome Brown	18,264	4,674	448	Resulfont Brown	16,781	5,255				
159a	Pygoreux Fast Black T	16,000	3,522	452	Benzo Fast Blue (V.M.)	26,559	8,439				
160	Fast Brown N.	67,531	6,200	462	Direct Deep Black E	32,830	5,032				
161	Fast Red	46,258	4,463	467	Congo	14,745	22,206				
162a	Carminoine (V.M.)	17,107	2,427	468	Cotton Black (V.M.)	61,218	9,044				
163b	Chrome Blue (V.M.)	53,404	19,874	469a	Chloramine Black	20,095	5,278				
164a	Diamond Blue R.	20,117	3,500	469b	Chloramine Black (V.M.)	19,505	3,951				
164b	Amaraiah	73,723	9,429	474	Oxamine Green B.	23,832	5,134				
168b	Wool Red (V.M.)	11,947	2,283	474a	Diamine Green (V.M.)	53,268	8,318				
169	Cochineal Red	23,984	3,669	475a	Benzenamine Brown 3	16,988	2,470				
173a	Lithol Red (V.M.)	67,515	5,029	477a	Naphthamine Brown (V.M.)	48,734	9,452				
177	Mordant Yellow	55,093	11,280	478	Columbia Green	24,749	4,723				
177a	Anthracene Yellow	16,650	3,011	482	Direct Green (V.M.)	19,313	4,291				
177b	Saline Yellow	23,068	3,536	485a	Benzo Brown (V.M.)	41,905	7,125				
180	Erichrome Blue Black BC	43,880	8,485	490a	Cotton Brown (V.M.)	23,975	5,207				
181	Sulfine Blue	10,660	10,660	Unclassified Azo Colors.							
184	Erichrome Black A	96,570	13,530	A 6	Chrome Fast Black (V.M.)	76,451	10,172				
185	Anthracene Chrome Black	51,577	7,869	A 12	Columbia Brown (V.M.)	20,793	3,073				
188	Sulfone Acid Blue R.	45,038	11,372								
189	Sulfone Acid Blue B.	35,112	8,813								
198	Thiazine Yellow	29,879	8,410								
211	Resorcin Brown	13,189	2,549								

Serial No.	Commercial Name.	Lbs.	Invoice Value.	Serial No.	Commercial Name.	Lbs.	Invoice Value.	Serial No.	Commercial Name.	Lbs.	Invoice Value.				
Class I (Under 100,000 lbs.)															
U695	Blue (V.M.)	61,949	9,509	436a	Dianol Black	112,095	12,635	131	Metanil Yellow	284,606	46,614				
U701	Calcutta Blue 2	13,657	3,627	442a	Direct Black (V.M.)	145,738	11,831	157	Diamond Black	285,947	37,065				
U708	Meridian Black A.E.	26,669	4,669	455a	Columbia Black (V.M.)	143,956	26,125	173	Lithol Red R	214,448	18,550				
U711	Omega Chrome Cyanine R	15,157	3,316	462f	Carbide Black (V.M.)	190,394	31,697	174b	Scarlet	209,281	20,472				
U716	Alpha Black J.C. 6	21,001	3,019	A169	Benzo Fast Black L	100,268	22,846	303a	Paper Yellow (V.M.)	264,443	45,320				
U731	Cachou (V.M.)	56,991	3,430	A382	Oxy Diamine Black (V.M.)	146,629	24,836	436	Columbia Black	290,902	41,563				
U744	Alizarine Black M.	18,979	1,986	A387	Oxy Diaminogen (V.M.)	139,118	26,532	463	Cotton Black E	248,567	34,602				
U770	N.L. Blue (V.M.)	10,047	2,126	495	Malachite Green	178,831	43,363	615	Methyl Violet	255,063	63,183				
Class II (100,000 to 200,000 lbs.)															
34	Chrysoline R	105,946	16,852	443	Patent Blue	114,631	49,945	636	Alkali Blue	286,531	117,365				
48	Alizarin Yellow	144,761	11,118	558	Victoria Blue R	109,527	31,817	748	Hydron Blue (G. R.)	292,729	33,655				
145	Orange II	127,550	10,116	563a	Wool Blue (V.M.)	173,904	18,406	778	Alizarin (Synthetic)	202,392	20,465				
163	Azo Rubine	160,252	25,409	606	Phosphine	101,858	30,442	806a	Alizarin Black (V.M.)	229,500	33,275				
181b	Salicic Black (V.M.)	177,203	26,945	659	Methylene Blue (V.M.)	185,738	72,619	Class IV (300,000 to 400,000 lbs.)							
183	Eriochrome Black T	129,550	23,447	698	Nigrosine, Soluble in Spirit (V.M.)	136,540	23,435	274	Diaminogen	305,944	56,201				
217d	Naphthylamine Black (V.M.)	122,561	12,240	774	Alizarin Black S, SR, NR	136,461	9,936	275	Diamond Black	351,582	55,020				
217f	Anilol Black (V.M.)	105,095	10,962	782	Alizarin Brown (V.M.)	110,211	30,907	363	Benzo purpurine 4 B.	341,724	45,233				
220	Palatine Black	148,203	15,169	789	Anthracene Blue WR	107,778	13,622	A396	Cotton Black (V.M.)	300,173	44,567				
220b	Wool Black (V.M.)	110,244	16,568	807	Alizarin Black S	198,491	19,902	A432	Lake Red (V.M.)	349,280	11,682				
227	Brilliant Croceine	123,058	20,333	808a	Alizarin Green (V.M.)	124,095	58,491	700	Nigrosine, Sol. in Water	394,718	58,903				
257	Sulfon Cyanine	128,944	21,118	833	Indanthrene Blue RS	187,379	56,532	803a	Alizarin Blue (V.M.)	302,319	69,712				
266	Naphthylamine Black	152,141	21,903	U390	Wool Black (V.M.)	118,791	20,453	Class V (400,000 to 500,000 lbs.)							
268a	Naphthol Black (V.M.)	131,890	19,436	U396	Wool Black (V.M.)	108,863	14,781	30xamine Black	417,422	57,464					
284	Bismarck Brown 2 R	171,221	32,241	Class III (200,000 to 300,000 lbs.)				842	Auramine	449,276	107,887				
304	Chrysophenine	148,406	40,466	7	Naphthol Yellow	250,409	24,702	842	Indanthrene Blue GCD	478,980	169,780				
333b	Diamine Black (V.M.)	171,221	19,434	23	Tartrazine	265,781	53,137	Class VI (over 500,000 lbs.)							
424	Chicago Blue 6 B.	116,560	32,417					462a	Direct Deep Black E	862,601	110,009				
												46a	Zambell Black (V.M.)	629,359	107,669
												720	Sulfur Blacks (V)		
												734	Indigo, Synthetic	8,907,359	1,929,733

of the calendar year 1914. No serious interference in the output of American colors occurred until after the beginning of 1915.

With the cordial co-operation of the Secretary of the Treasury, all the invoices for the year in question were sent by the collectors of customs at the various ports of entry to a central point, where the essential data were transcribed. These include weight, value and price. Some 37,500 different transcripts, each covering these three items, were necessary.

These entries are found under 5,674 heads, each representing a distinct commercial designation. It must not be inferred, however, that this number of different colors comes into consideration. Many standard dyes are manufactured by several firms in the same country as well as in various countries. Frequently, some or all of the competing manufacturers use entirely different trade names for identical wares.

Thus, the red color, known chemically as sodium α -naphthalene azo- α -naphthol-disulfonate, is manufactured under the name of Palatine Red by the Badische Co. The Bayer Co. sells it under the name of Naphthorubine. Primuline is encountered commercially as Polychromene, Thiochromogen, Aureoline and Sulfine. Malachite Green, a favorite color, is found under 38 different designations, few representing even slight variations in the exact chemical composition.

The reduction of this extensive vocabulary to the limits of the list given in the census has required highly specialized editing. It is hoped that the arrangement and the full use of synonyms are such as to render the published results of the greatest utility, not only to all engaged in the manufacture of artificial dyes, and especially in planning for the establishment of a comprehensive American color industry, but also to all dealers in the wares and to all consumers of dyeing materials.

All three of these categories have hitherto been indebted to the painstaking labors of several prominent German color chemists, notably of Gustav Schultz and

Paul Julius, for complete and detailed classifications of the coal-tar dyes in current use. The carefully elaborated "Farbstofftabellen," devised by the two authors, reached a fifth edition in 1914. These "tables," divided into groups according to chemical relationship, give for every artificial dye of known composition or preparation the commercial designation, the scientific name, the chemical formula, the most advantageous process for technical production, physical and chemical properties, methods of application, tests and full references to patents and literature. They have for years been the *cadre mecum* of all connected with the manufacture of colors, their commerce, and their manifold uses.

It has remained for a bureau of our Government to supplement the work of the German duo, by adding the all-important factor of quantity. The complete exposition of the exact amounts of the many synthetic dyes required to meet the almost numberless needs of a population of over 100,000,000, portrays approximately the relative demands of all other nations with highly organized textile and allied interests. The young American dyestuff industry, now in a position to expand rapidly and to embrace in its scope the great majority of the colors in current use, will naturally find in it a sure guide for co-ordinating the diverse phases of manufacture, establishing the capacity of units, and shaping all plans for harmonious expansion.

More than this, it will be of almost equal value to those seeking to create the national coal-tar industries of Great Britain, France, Russia and Italy. Even the newly organized industry in Japan may profit from its summaries, although in a less pronounced degree, on account of the widely divergent taste for colors between the Orient and the Occident.

Should China plan to manufacture her own coal-tar dyes, but little help could be secured from this compilation in formulating schemes for installing plants. Synthetic indigo constitutes two-thirds of the

Chinese consumption of artificial colors. It enters to the extent of 14 per cent into the Japanese imports of dyestuffs, and forms but 10 per cent of the American consumption.

One of the first results of the compilation of this census was to show how exceedingly vague an idea of the extent to which synthetic dyes are consumed in the United States prevailed in commercial and manufacturing circles. Those most closely in touch with the branch have estimated hitherto that the annual American consumption of coal-tar colors did not exceed 20,000 tons. As a matter of fact, it is nearly one-half again this amount—more exactly, 29,000 short tons.

SUMMARY OF THE MOST IMPORTANT COLORS IMPORTED.

It has seemed desirable, in the interest of American chemists who are now studying closely the problems connected with the creation of a national dyestuff industry, to prepare a summary of the more important synthetic colors currently imported into this country and compiled systematically, in the complete census of dyes consumed in the United States, now in press.

The list prepared (pages 1042, 3 and 4) includes practically all colors, the annual importation of which, during the fiscal year 1913-14, exceeded in amount 10,000 lbs. These colors, for the sake of classification, are divided into six groups, according to the amount of the importation.

PRICES OF DYES.

The values of the different colors imported from Europe are taken directly from the invoice entries. The prices varied but little during the course of the fiscal year 1913-14. They are on file in the Bureau of Foreign and Domestic Commerce. It did not seem necessary to reproduce them in full in the enumeration of colors. The average price for the year, in the case of any dye, is easily ascertained by a simple act of division.

In most cases the values stated represent the lowest possible estimate of wholesale cost which can be placed upon the wares in question. The bulk of the importations is shipped from the great manufacturing firms of Germany, Switzerland and England, to their agents in this country. The latter are ordinarily incorporated American companies, bearing essentially the same names as the European houses which they represent, and may be practically under the control of the latter, if not financed by them directly.

Under these circumstances and in view of the exceptional difficulty of ascertaining market values for the highly differentiated gradations of quality in the thousands of brands of artificial colors, there was a strong temptation to place the lowest possible values upon wares subject to an *ad valorem* duty of 30 per cent.

It is doubtful in many cases, therefore, whether the values published in the following lists are fully equal to those against which American manufacturers of colors would contend, should all the factors, falling

under the head of "unfair competition," be eliminated in the international trade in synthetic dyes. In these values there is a slight element of variability and uncertainty, based upon the lack of uniformity in invoicing colors.

In some cases—probably the majority—the prices and values are net, not covering charges for containers and packing, freight, and insurance to seaport, consular certification, minor shipping charges at point of departure and at seaport. Wares shipped by the "Badische Co.," the Berlin "Actien-Gesellschaft," the "Cassella Co.," the "Griesheim-Elektron," and the "Chemikalienwerk-Griesheim" are usually invoiced in this manner.

Other firms, such as the "Bayer Co.," the "Sandoz Co.," "Carl Jäger," and "Beyer and Kegel," include in their prices the cost of containers and packing, freight and insurance to seaport, consular certification, and minor shipping charges. In other words, their prices are f. o. b. ocean steamers at Hamburg, Bremen, Rotterdam, Antwerp, etc.

It has not been possible, on account of time limitations, to estimate this small factor in the case of each shipment and make the accompanying correction in value so as to have actual uniformity in the basis of valuation. The element of quantity is the dominant feature in this work, and in view of what is stated above, very elaborate calculations of values would be of doubtful utility.

COST OF PACKING, FREIGHT, INSURANCE, ETC.

It is well, however, to know with some approximation to exactness the extent and nature of the charges incident to the importation of European coal-tar colors into the United States. They are as follows:

Consular certification—A fee of \$2.50 for all invoices covering shipments, the value of which exceeds \$100.

Freight to seaport—This is quite variable, depending upon the distance to be traversed and whether rail or water transportation is employed. Rates per pound (net) of color are \$0.00125 from Berlin; \$0.0056 to \$0.0071 from Basel; \$0.0008 to \$0.00216 for points on the Rhine.

Insurance, in transit to seaport—Rates vary from \$0.0007 to \$0.0016 for each dollar of invoice value.

Shipping charges—The item appears occasionally and ranges from \$1 to \$2 for each \$1,000 of an invoice.

Ocean freight—Customary rates from European ports, such as Hamburg and Antwerp to New York, were, prior to the war, \$0.75 per metric ton (gross weight) for most of the coal-tar dyes, and \$7.91 for certain categories, such as sulphur black and other sulphur colors.

Several large invoices of colors showed an average rate for ocean freight per net pound of dyestuff, of \$0.00471, ranging from \$0.004125 to \$0.00530. Through freight from Frankfort to New York on a

large and varied assortment of artificial dyes was at the rate of \$0.00755 per net pound of colors.

On an average, 1 lb. of color (net) is represented by 1.165 lbs. gross weight, the tare per pound ranging from 0.155 to 0.174 lb. on shipments of some size.

Marine insurance—Insurance on large shipments of dyes from Frankfort to New York, covering both inland and marine insurance, was equivalent to \$0.000916 per pound (net) of colors. This represented \$0.00497 on each dollar of value, or about 0.5 per cent on the value. Shipments by another company, located on the Rhine, averaged 0.3 per cent.

Packing—There is some diversity in the average cost of containers. This item ranges from \$0.00459 to \$0.00863 per pound (net) of color in a number of large invoices. A fair average would be \$0.00651 per net pound.

Some of the more expensive colors are shipped in tin boxes, packed in cases holding 100 lbs. (net). Cases cost \$0.48. The charges for tins are as follows: 1 lb., 48c; 5 lbs., 96c; 10 lbs., 155c; 25 lbs., 32c. Kegs, containing 100 lbs., cost usually \$0.95, but range in value from \$0.63 to \$1.14. Casks hold ordinarily about 500 lbs. The net contents range, however, from 415 to 595 lbs. In four large shipments the average net weights were 442, 469, 480, and 531 lbs. The general average was 480 lbs. The average price of casks is \$1.90. They range, however, in cost from \$1.55 to \$3.24.

On an average the importation of European colors to New York costs \$0.014 per net pound for packing and transportation (packing \$0.0065, transportation \$0.0075), and \$7 per \$1,000 of value for insurance and incidental charges (insurance \$5, shipping charges and consular certification \$2).

American consumers of coal-tar colors, who may wish to compare the prices paid by them two or three years ago for European wares with the prices based upon the values furnished in this report, can add to the prices calculated from these values the cost of the above items. In addition there comes the duty of 30 per cent *ad valorem* on all artificial colors, except indigo and its derivatives, and colors made from anthracene (largely alizarin) and carbazole, which were exempt from duty under the late tariff. This duty is levied upon the combined cost of dye and its containers. Furthermore, the normal cost of handling, storing, and distributing, in the importing houses, is to be added. The difference between the sum total of these various items and the current price for a given color represents the profit made by the importer.

ARTIFICIAL COLORS MANUFACTURED IN THE UNITED STATES.

The manufacture of coal-tar colors in the United States has been in existence for some 37 years. Prior to 1915 it had never become a factor of importance in supplying the American market. The reasons for this slowness of development have been presented in

detail in the monograph published in 1915 by the Bureau of Foreign and Domestic Commerce, entitled "Dyestuffs for American Textile and Other Industries" (Special Agents' Series No. 96).

The American manufacture was confined almost entirely to the "assembling" into finished dyes of coal-tar intermediates imported from Europe, chiefly from Germany. In its entirety it represented less than one-tenth of the activity to be encountered in any one of the larger companies producing synthetic colors in Germany and Switzerland.

STATUS OF THE DOMESTIC PRODUCTION IN 1914.

The status of the industry for the calendar year 1914 is shown by the following tabular statement prepared by the Bureau of the Census:

Number of establishments.....	7
Persons engaged in manufacture.....	528
Salaried employees	130
Wage earners (average number).....	398
Primary horse power.....	1,376
Capital	\$3,386,212
Services	\$ 529,070
Salaries	\$ 273,633
Wages	\$ 255,437
Materials	\$1,936,982
Value of products.....	\$3,596,795
Coal-tar colors— ..	
Pounds	6,619,729
Value	\$2,470,096
All other (including medicinal coal-tar products to value of \$174,598).....	\$1,126,699
Value added by manufacture.....	\$1,659,813

The scope and extent of the manufacture carried on prior to the war by the seven American companies engaged in this branch was summarized under their respective names. No attempt has been made to estimate the annual output of the individual colors made in the American factories, as it fluctuated largely from year to year.

In nearly all cases the character of the manufacture has been vastly affected by the conditions prevailing since 1914. As a rule the variety of colors has been diminished while the output has been vastly augmented.

The number of employes has been notably augmented. In general, it has been quintupled. In one case the force is 50 times greater than in 1914.

THE SCHOELLKOPF ANILINE AND CHEMICAL WORKS (INC.).

This firm, located at Buffalo, N. Y., was founded in 1879, and is the oldest American company in this industry. A number of dyestuffs in current use originated in its laboratories. It has shown a commendable degree of enterprise in maintaining its position for over a third of a century, frequently under conditions of a most discouraging nature. It has also earned the grateful recognition of a multitude of American consumers of dyes by swiftly enlarging the capacity of its works so as to alleviate materially the severity of the dyestuff famine to which our textile and allied interests have been exposed.

The annual output of this firm constituted about one-half of the American production of coal-tar dyes. The following colors were currently manufactured before

the war. The serial numbers correspond to those given in Schultz's "Farbstofftabellen":

STILBENE AND PYRAZOLONE DYES.	211 Resorcin Brown.
9 Direct Yellow F.	217 Buffalo Black NB.
9 Direct Yellow 2 RF.	220 Buffalo Black PY extra.
23 Wool Yellow extra conc.	227 Croceine Scarlet MOO.
TRIPHENYL-METHANE DYES.	257 Buffalo Cyanine R.
512 Fuch sine.	257 Buffalo Cyanine 3 R.
512 Fuch sine TR.	261 Buffalo Black 8 B, 10 B.
513 Fuch sine NB.	266 Buffalo Black AD.
521 Spirit Blue, red shades.	268 Buffalo Black EA.
521 Spirit Blue, green shades.	269 Buffalo Black 4 B.
524 Acid Magenta.	272 Buffalo Black 2 B.
536 Alkali Blues, red shades.	275 Buffalo Chrome Black BWN.
536 Alkali Blues, green shades.	283 Bismarck Brown Y.
537 Paper Blues, red shades.	284 Bismarck Brown 53.
537 Paper Blues, green shades.	303 Brilliant Yellow C.
537 Paper Blue, 6 G super.	307 Congo Red 4 B.
XANTHONE DYES.	311 Erie Orange 2 R.
587 Eosine.	612 Buffalo Direct Garnet R.
AZINES.	313 Buffalo Direct Crimson B.
679 Safranin Y extra.	320 Bordeaux extra.
680 Safranin 6 B.	326 Niagara Violet 2 B.
684 Brilliant Safranin R.	327 Niagara Blue R.
699 Nigrosines from aniline (indulines).	327 Niagara Violet 3 R.
700 Nigrosines from nitrobenzol.	333 Diazine Black H extra.
AZO DYES.	336 Niagara Blue GW, HW, RW.
31 Oil Yellow A.	337 Niagara Blue B, 2 B.
31 Oil Yellow 2025.	342 Buffalo Direct Yellow CG extra.
33 Chrysoidine Y extra.	343 Niagara Fast Red FD.
33 Chrysoidine crystals.	344 Erie Direct Brown 3 RB.
36 Oil Orange 2311.	362 Buffalo Direct Orange R.
36 Oil Yellow 2338.	363 Buffalo Direct Red 4 B.
37 Croceine Orange Y.	375 Buffalo Direct Violet 4 R.
38 Crystal Orange 2 G.	386 Niagara Blue BR.
64 Buffalo Fast Crimson G.	392 Buffalo Direct Orange Y.
66 Buffalo Fast Crimson R.	394 Buffalo Direct Yellow CRR extra.
68 Oil Yellow 2681.	405 Buffalo Direct Cardinal 7 B.
70 Croceine Orange R.	410 Buffalo Direct Blue G extra.
82 Xylidine Scarlet.	424 Niagara Blue 6 B.
83 Cumidine Scarlet.	426 Niagara Blue 4 B.
94 Buffalo Flame B.	436 Panama Black R extra.
95 Buffalo Flame G.	436 Panama Black 3 G extra.
105 Sudan Brown S.	441 Niagara Black Blue R.
110 Buffalo Rubine.	462 Erie Direct Black G extra.
112 Azo Bordeaux.	463 Erie Direct Green ET.
126 Indoline Blue.	464 Erie Direct Green WT.
134 Metanil Yellow.	474 Erie Direct Green MT.
141 Azo Yellow.	477 Erie Direct Brown GR.
141 Azo Yellow A 5 W.	477a Erie Direct Brown GB.
143 Resorcin Yellow.	488 Erie Direct Brown RF, 2 RF.
145 Orange A.	
147 Buffalo Fast Fuch sine B.	
151 Orange R.	
161 Fast Red conc.	
161 Fast Red S conc.	
163 Azo Rubine extra.	
168 Wool Red 40 F.	
169 Brilliant Scarlet 3 R.	
188 Buffalo Fast Blue R.	
AZO DYES (concluded).	
189 Buffalo Fast Blue B.	

THE HELLER AND MERZ CO.

This firm, located at Newark, N. J., stands second in point of seniority and importance. Its annual output of coal-tar colors was estimated at slightly less than one-quarter of the country's production. It has catered very largely to the needs of the paper trade. In addition to organic dyestuffs, it has manufactured large quantities of mineral colors, notably ultramarine. The equipment for the production of coal-tar dyes has been largely augmented during the past year.

The following artificial colors were currently man-

ufactured in 1914 (serial numbers of Schultz's Farbstofftabellen):

AZO DYES.	TRIPHENYL-METHANE DYES.	XANTHONE DYES.
33 Chrysoidine.	512 Fuch sine.	587 Eosine.
145 Orange 11.	515 Methyl Violet.	AZINES.
283 Bismarck Brown.	536 Alkali Blue.	698 Nigrosine.
	537 Soluble Blue.	700 Nigrosine.
	538 Methyl Blue.	water-soluble.
	539 Acid Blue.	

THE BAYER CO. (INC.)

This company owns works at Rensselaer, N. Y., where several of the staple colors and medicinal products of the Farbenfabriken vormals Friedr. Bayer & Co., of Leverkusen, Germany, are manufactured on a scale of some importance. The output of coal-tar dyes prior to the war constituted somewhat less than one-fifth of the entire production. The expansion during the past year and a half has not been as pronounced as in the case of the other establishments.

Prior to the war the company manufactured the following colors:

AZO DYES.	TRIPHENYL-METHANE DYES.	AZINES.
33 Chrysoidine.	512 Fuch sine.	698 Nigrosine.
283 Bismarck Brown.	536 Alkali Blue.	699 Induline.
	537 Soluble Blue.	700 Nigrosine.
		water-soluble.

W. BECKER'S ANILINE AND CHEMICAL WORKS (INC.)

This company, founded in 1912, is located at Brooklyn, N. Y. Prior to the war it specialized on alizarin substitute colors. The annual output was modest, estimated at about 180 tons. During the past 18 months the plant has been rapidly enlarged. Today it is second in importance as a factor in the domestic color industry.

The following colors were manufactured regularly prior to 1915:

AZO DYES.	XANTHONE DYES.
18 Alizarin Yellow.	599 Chrome Blue R, powder and paste.
187 Acid Fast Blue SB.	OXAZINE DYES.
83 Ponceau 3 R.	626 Chrome Blue B, paste and powder.
145 Orange 11.	
163 Azo Rubine WB.	333 Diazo Black BHN.
166 Fast Red A.	337 Direct Blue WBB.
188 Acid Fast Blue SR.	342 Direct Yellow WH.
	410 Benzazurine WB.
	426 Direct Sky Blue B.

THE CENTRAL DYE-STUFF CO.

This company, located at Newark, N. J., was founded in 1898. The output was not large, possibly 4 per cent of the country's production. It included, however, several dyes of importance for the textile industries. The plant has been notably enlarged during the past year.

Prior to the war the following colors were currently manufactured:

AZO DYES.	AZINES.
31 Amido-azo-benzene.	161 Fast Red.
33 Chrysoidine.	163 Azorubine.
37 Croceine Orange.	168 Amaranth.
68 Amido-azo-toluene.	174 Scarlet.
112 Bordeaux B.	223 Sudan III.
145 Orange 11.	229 Sudan IV.
	283 Bismarck Brown.
	697 Enduline.
	698 Nigrosine.

THE CONSOLIDATED COLOR AND CHEMICAL CO.

This company, located also at Newark, N. J., manufactured for some years prior to the war less than 100 tons annually of colors. The following colors for textile works were currently produced.

58 Alizarin Yellow R. 168 Fast Red. 144 Naphthol Orange.

In addition, a certain variety of colors for pigments, especially alizarin, para and scarlet lakes, and for use in paper making, were regularly manufactured. During the past year the plant has been greatly enlarged. It is at present an important center of production.

HUB DYESTUFF AND CHEMICAL CO.

This company, located at South Boston, Mass., manufactured on a modest scale, for a few years, prior to 1915, 58 Alizarin Yellow R.

IMPORTATION OF COAL-TAR CRUDES AND INTERMEDIATES.

As stated above, the synthetic colors manufactured in the United States prior to 1915 were made almost exclusively from intermediate coal-tar products imported from Europe. Germany was the chief source. A considerable amount, however, was of British origin.

A single noteworthy exception is found in the case of aniline. The American manufacture of this all-important intermediate was organized in 1910. The annual output had attained about 900 short tons in 1914—the product of a single establishment. At present aniline is regularly manufactured by over 30 companies and the annual output is in excess of 16,000 short tons.

In connection with the preceding enumeration of the artificial dyes currently produced in the United States prior to the war, it is of considerable importance to know what coal-tar crudes and intermediates were imported for use in their manufacture and, further, the quantity and value of each crude and intermediate. This information is furnished in the following tabular statement based upon the importations for the fiscal year ending June 30, 1914:

IMPORTS OF COAL-TAR CRUDES, FISCAL YEAR 1913-14.

	Pounds.	Value.
Benzene	131,211	\$4,247
Toluene	199,088	7,892
Xylene	30,681	1,722
Naphthalene	3,880,108	70,428
Anthracene and anthracene oil	32,175	531,535
Phenol (carbolic acid)	8,393,216	109,146
Phenol, ref.	104,361	16,139
Cresol	59,271,677	3,822,919
Creosote oil (gallons)		
Total		\$4,596,203

An exceedingly small part of the above-mentioned coal tar crudes was utilized in the manufacture of artificial colors. The creosote oil was employed in the preservation of timber. The phenol served chiefly as a disinfectant and antiseptic. The chief use of naphthalene was in the familiar form of "moth balls."

During the calendar year 1913, according to official German records, the following coal-tar crudes were imported into the United States from Germany: Naphthalene, 7,900 short tons; carbolic acid (pure and

crude), 1,320 short tons; cresol, 220 short tons; creosote oil, 17,000 short tons.

IMPORTS OF COAL-TAR INTERMEDIATES, FISCAL YEAR 1913-14.

The values given are net invoice values of European manufacturers and do not include cost of containers, etc.

Intermediates.	Pounds.	Value.
Nitro Compounds—		
Nitro-benzene	1,087,911	\$ 59,835
Dinitro-benzene	164,650	10,399
Nitro-toluene	6,670	359
<i>o</i> -Nitro-toluene	42,482	2,969
Dinitro-toluene	547,701	36,660
Trinitro-toluene	57,242	13,242
<i>a</i> -Nitro-naphthalene	2,247	165
<i>m</i> -Nitraniline	3,527	1,037
<i>p</i> -Nitraniline	506,961	67,638
Methyl-nitraniline	599	135
Nitro-toluidine	10,874	3,415
<i>m</i> -Nitro- <i>p</i> -toluidine	10,513	4,200
<i>o</i> -Nitro- <i>p</i> -toluidine	20,737	6,524
<i>p</i> -Nitro- <i>o</i> -toluidine	30,642	9,723
<i>p</i> -Nitro-phenol	4,780	774
Carboxylic Acids—		
Benzoic acid	278,896	51,701
Phthalic acid	63,574	15,597
Tetrachloro-phthalic acid	1,102	659
Ethyl- <i>p</i> -toluene-sulfonic ester	21	19
Primary Amines and Derivatives—		
Aniline oil	1,444,772	116,628
Aniline salts	3,083,467	222,728
Acetanilide	1,060	164
<i>p</i> -Amido-acetanilide	5,568	1,365
<i>p</i> -Sulfanilic acid	4,477	257
Toluidine	108,835	14,161
<i>a</i> -Toluidine	309,595	27,361
<i>m</i> -Toluidine	174	25
<i>p</i> -Toluidine	24,686	4,764
Xylidine	18,600	2,167
<i>p</i> -Phenetidine	33,093	11,925
Naphthylamine	25,573	2,705
<i>a</i> -Naphthylamine	112,226	10,620
Naphthylamine-sulfonic acid (constitution unknown)	500	161
<i>a</i> -Naphthylamine-sulfonic acid (L acid; 1,5)	2,832	497
<i>a</i> -Naphthylamine-sulfonic acid (Cleve's acid; 1,6 or 1,7)	5,493	711
<i>a</i> -Naphthylamine-disulfonic acid (Freund; 1,3,6)	5,246	604
<i>β</i> -Naphthylamine	5,973	997
<i>β</i> -Naphthylamine- <i>a</i> -sulfonic acid (<i>a</i> or Badische acid)	23,265	7,579
<i>β</i> -Naphthylamine- <i>β</i> -sulfonic acid (<i>β</i> or Brönnner's acid)	2,316	495
<i>β</i> -Naphthylamine-disulfonic acid (<i>a</i> or R acid; amido-R-salt; 2,3,6)	46,267	4,495
<i>β</i> -Naphthylamine-disulfonic acid (<i>γ</i> or G acid; amido-G-salt; 2,6,8)	3,603	230
Secondary Amines and Derivatives—		
Dimethyl-aniline	48,642	7,045
Diphenylamine	55,556	9,042
Ethyl- <i>a</i> -naphthylamine	1,102	338
Ethyl- <i>β</i> -naphthylamine	375	190
Phenyl- <i>a</i> -naphthylamine-8-sulfonic acid	9,139	2,860
<i>p</i> -Tolyl- <i>a</i> -naphthylamine-8-sulfonic acid	1,097	568
Diamines and Derivatives—		
Phenylene-diamine	37,907	7,704
<i>p</i> -Phenylene-diamine	11,088	3,414
<i>m</i> -Tolylene-diamine	133,355	25,582
<i>m</i> -Tolylene-diamine-sulfonic acid (1,2,4,6)	2,277	835
Benzidine	55,245	16,991
Dianisidine	10,656	4,217
Phenols and Derivatives—		
Salicylic acid	18,821	4,425
Acetyl-salicylic acid	22,841	11,873
Resorcin	61,624	18,175
Hydroquinone	66,596	25,140
Pyrogallol	23,615	20,476
Gallic acid	61,635	20,429
Naphthols (<i>a</i> and <i>β</i>)	70,469	4,193
<i>a</i> -Naphthol	44,089	2,271
<i>a</i> -Naphthol-5-sulfonic acid (L or Cleve's acid; 1,5)	25,126	5,026
<i>a</i> -Naphthol 3,6,8-trisulfonic acid (1,3,6,8)	6,443	1,344
<i>β</i> -Naphthol	1,030,268	74,238
<i>β</i> -Naphthol-monosulfonic acid (constitution unknown)	32,852	5,998

β -Naphthol-7-sulfonic acid (F salt; 2,7).....	1,996	382
β -Naphthol-6,8-disulfonic acid (G acid; 2,6,8).....	11,624	1,404
1,8-Dioxy-naphthalene-4-sulfonic acid ...	2,178	1,056
8-Oxy-naphthoic acid.....	2,359	972
β -Oxy-naphthoic anilide (Naphthol AS).....	1,997	1,218
Amido-Phenols and Derivatives—		
<i>o</i> -Amido-phenol.....	625	223
Sodium picramate.....	5,297	1,485
Oxy-nitraniline.....	200	32
Diamido-phenol.....	441	391
<i>p</i> -Amido-phenol.....	10,631	1,684
<i>p</i> -Amido-phenol hydrochloride.....	652	189
<i>p</i> -Amido-salicylic acid.....	9,188	2,996
Methyl- <i>p</i> -amido-phenol sulfate.....	10,582	13,658
1,8-Amido-naphthol-3,6-disulfonic acid (H acid; 1,8,3,6).....	96,296	23,168
2,5-Amido-naphthol-7-sulfonic acid.....	1,153	445
Aldehydes and Quinones—		
Benzaldehyde.....	19,950	2,757
Oil of bitter almonds (benzaldehyde)...	7,525	21,954
Anthraquinone.....	25,193	4,676
Developers, Reducers and Indicators—		
Fast Blue Developer AD (amido-diphenylamine).....	100	39
Oxamine Developer H.....	11,096	2,119
Orange Developer R.....	701	376
Developer Z (phenyl-methyl pyrazolone).....	1,397	377
Phenolphthalein.....	14,076	14,090
Total.....	10,165,896	\$1,082,775

SUMMARY OF IMPORTS OF COAL-TAR PRODUCTS, 1913-14.

The coal-tar crudes and intermediates listed above, with the exception of aniline oil and salts, several acids, such as carbolic acid and salicylic acid, alizarin and colors derived from alizarin, anthracene and carbazole, indigo and its derivatives, and a few other compounds, such as antipyrine, aspirin, saccharin, and phenolphthalein, are included in the following summarized statement of the imports for consumption into the United States of coal-tar products, for the fiscal year ending June 30, 1914, published by the Bureau of Foreign and Domestic Commerce.

Imports designated by an asterisk (*) are for the period July 1 to October 3, 1913. Those designated by a dagger (†) are for the remainder of the fiscal year.

Coal-Tar Products—	Rate of duty.	Value.
Anthracene and anthracene oil.....	Free†	\$32,175.00
Colors or dyes, n. s. p. f.....	30 per cent	7,537,869.55
Do. (for use of the U. S.).....	Free	54.00
Dead or crosote oil (59,271,677 gallons).....	Free	3,822,919.00
All other, not medicinal and not colors or dyes, known as benzol, toluol, naphthalin, xylo, phenol, cresol, toluidine, xylin, cumidin, binitrotoluol, binitrobenzol, benzidin, tolidin, dianisidin, naphthol, naphthylamine, diphenylamin, benzaldehyde, benzylchloride, resorcin, nitrobenzol, and nitrotoluol; naphthylaminsulfoacids, naphtholsulfoacids and amidonaphtholsulfoacids and their sodium or potassium salts; amidosalicylic acid, binitrochlorbenzol, diamidostilbendisulfoacid, metanilic acid, paranitranilin, and dimethylanilin....	Free*	288,799.00
Distillates, n. s. p. f., not medicinal and not colors or dyes, benzol, naphthol, resorcin, toluol, xylo....	5 per cent†	138,636.00
Not medicinal and not colors or dyes, known as toluidine, xylin, cumidin, binitrotoluol, binitrobenzol, benzidin, tolidin, dianisidin, naphthylamine, diphenylamin, benzaldehyde, benzyl, chloride, nitrobenzol, and nitrotoluol; naphthylaminsulfoacids, naphtholsulfoacids, and amidonaphtholsulfoacids and their sodium or potassium salts; amidosalicylic acid, binitrochlor-		

benzol, diamidostilbendisulfoacid metanilic acid, paranitranilin, and dimethylanilin.....	10 per cent*	398,996.00
Do. (for use of the U. S.).....	Free	40,741.00
Naphthalene, phenol, and cresol....	Free†	195,713.00
All preparations of, not colors or dyes, and not medicinal, n. s. p. f.		
20 per cent*		162,864.00
All other products or preparations of, not colors or dyes, n. s. p. f.		
15 per cent†		496,548.13
Do. (for use of the U. S.).....	Free†	18,082.00
Total coal-tar products.....	(Free Dutiable)	\$4,398,483.00 8,734,913.68

IMPORTS OF INTERMEDIATES FROM GERMANY.

The official records of exports of intermediates from the German Empire to the United States show that the following quantities, in short tons, were shipped during the calendar year 1913:

Aniline oil and salts.....	2,640
Naphthol and naphthylamine.....	660
Anthraquinone, nitrobenzene, phthalic acid, resorcin, toluidine, etc.....	1,067
Benzoic acid, salicylic acid, and their sodium salts....	297

Total (short tons)..... 4,664

THE MARKS OF COAL-TAR COLORS.

The great diversity of marks employed by the different manufacturers of artificial dyes is a source of confusion and bewilderment to many, especially to those in the United States now taking an active interest in the evolution of a domestic coal-tar chemical industry, and but slightly familiar with the commercial features of this most complicated of all the varied branches of technology. As the subject has never been treated to any extent in the literature devoted to this industry, it seems desirable to furnish some information of a general character, as explanatory of the symbols used to discriminate between the different shades of dyestuffs.

Several of the managers and chemists of the leading firms in New York City devoted to the sale in this country of the dyes, tabulated in the census, have kindly responded to inquiries in this connection. The following excerpts from their letters furnish a fairly good portrayal of the few conventional features, and the general lack of uniformity characterizing the use of marks for coal-tar colors.

The customary designation of dyestuffs as practiced by the manufacturer, their representatives and the free-lances in the dyestuff business does not appear to be governed by any set formula. In the early days of the artificial-dyestuff industry, when dyes were few, the manufacturers designated distinct differences in shade by the letters B, R and G, signifying blue, red and yellow (gelb). Our French confreres used the corresponding B, R, J (jaune) and V (vert), which became familiar to dyers and dyestuff users. As dyes multiplied, differences in shade became more numerous and it became necessary to alter or to augment, as the case might be, the distinguishing marks. Consequently the marks 2 B, or 2 R, or 2 G, etc., became common and continue to this day.

No uniformity, however, exists between the corresponding marks of different concerns. For example, Chicago Blue 6 B, the lightest and brightest of the substantive blues, is designated in the schedule of another firm as 7 B, while among the products of still another firm it is indicated as FF.

Such marks serve to distinguish in a great measure the brands of different houses. One skilled in the art of buying and selling dyestuffs can, without great difficulty, distinguish a competitor's types among a variety of designations.

As far back as 1888 I went into this matter of type designations, discussed it with prominent dye agents, and was supplied by them at the time with comprehensive lists of their dyes and the meaning of their distinguishing letters. These demonstrated conclusively that each firm selling dyes was a law unto itself, so far as the commercial designation of its products was concerned.

Many individuals in and out of the textile industry and dabblers in tinctorial chemistry have entertained the idea that there was a key to a prescribed code of type designations which, in the hands of one possessing it, would unlock the numerous combinations of dyes required by individual customers, but this is not so.

We have, for example, a familiar instance of one of the smaller dyestuff firms, which designates its dye mixtures by numbers preceded by letters. These letters indicate the mixture books, Volume A, Volume B, Volume C, etc., and the number is that of the mixture. In order to duplicate the mixture, as in the case of a physician's prescription, one simply goes to the volume indicated by the letter and picks out the corresponding number. For all time that number holds good for one particular customer. No real trade secret is divulged by communicating this bit of information.

The letter X does not necessarily mean "extra," whatever "extra" is. In the codes of some firms probably it does mean "extra," presumably higher strength or greater brilliancy or solubility. In other cases it may designate the region where certain dyes are sold. NY, for example, indicates brands of colors prepared especially for the American market (New York).

The whole subject of dye designations is so complex that it becomes a hopeless problem to untangle. General references to it in literature are scarce, for the reason that there is nothing definite to say upon the subject. It is much like patent medicines; the medical trade has not formulated a code to designate such remedial agents.

Some dyestuffs are differentiated from others by appended letters to indicate their source, or the materials of which they are prepared. For instance, one of the well-known commercial types of Methylene Blue—especially Methylene Blue SZ—of no particular merit as to shade, possesses properties peculiar to itself an account of having been prepared free from zinc (sans zinc).

From the foregoing it is easily realized that the matter of commercial designations of dyes is very complex. While there are standards, i. e., established types of individual dyes, such as those enumerated in the Schultz tables, from which millions of combinations are possible, every dyestuff firm has thousands and thousands of these combinations upon their books. Each is necessarily designated by some intelligible and comprehensive system in order to guard against errors and mistakes in compounding when called for.

Many well-known types of "straight" dyes as produced by the manufacturer are, *per se*, of little value when used alone. Their value is brought out when used in combination with other dyes, and this is the strong point of many valuable mixtures that under no circumstance can be replaced by "straight" dyes. While we prefer to use straight or unmixed colors, we are frequently compelled to make use of mixtures, the value of which for dyeing purposes far outweighs the usefulness of the individual components when used separately. Such mixtures, of necessity, must be designated by different letters or numbers, to prevent confusion. A common instance of this is the very extensive series of combination shades, of great value, produced with the fast reds and azo scarlets, which may or may not be modified in tone by the judicious admixture of acid violets.—L. J. M.

* * * * *

There is no uniform practice and not much of a system in the marks which are used to distinguish the different brands

of dyestuffs. This fact may seem rather strange, but it may be readily understood if one realizes that all dyestuff concerns have manufacturing and selling ends of the business—two loosely connected departments. The dyestuff is sent from the manufacturing department to the dyehouse, which is connected with the selling department. Both the dyehouse and the selling department are kept in ignorance regarding the chemical nature of any new product which is brought out. The same has, therefore, to be classified according to its shade and its dyeing properties. The result is that in many cases the dyer identifies a color with a group of others having similar dyeing properties but which, in fact, are chemically entirely different. The leading principle in naming the colors is less one of general classification than to furnish the salesman of a special factory with some hint as to the dyeing properties of any given color.

In most cases it is understood, for instance, that the letter B stands for "bluish." Hence, 2 B, which is equivalent to B B, denotes a still bluer shade. G means "greenish" or "yellowish;" R, "reddish;" V, "violet." Apart from these few cases of uniform practice the marks are open to all kinds of explanation. The mark L, for instance, may mean "soluble," or "fast to light," or even may stand for Ludwigshaven, which means that the color in question is identical with a well-known product of the Badische Co. at Ludwigshaven. In the same way C may stand for "Cassella" (Leopold Cassella & Co., Frankfurt); H for "Hoechst" (Farbwere v. Meister, Lucius & Brining, Hoechst a. M.); E for "Elberfeld" (Farbenfabriken v. Friedr. Bayer & Co., Leverkusen, formerly at Elberfeld), and B or A for "Berlin" (Actien-Gesellschaft für Anilin-Fabrikation, Berlin). All refer to types against which the competitive products have been standardized.

The word "extra" indicates either a special shade or a special concentration. It is a rule with us that our "extra" marks are more concentrated than the single brands, which otherwise bear the same name and mark. The letter X is used by other firms in the same way as our "extra," for higher concentrations, without, however, giving any definite information regarding the proportionate strength.

Many suggestions have been made in order to do away with this rather confusing habit of classification, but so far without success. The reason is that the selling staff on the one hand, and the millman on the other hand, are not expected to possess much chemical or coloristic knowledge. Such knowledge only would enable them to benefit from a more complicated and scientific system.—A. M.

* * * * *

It is a pretty well-established practice among dye manufacturers to use certain marks and letters in connection with the name of any color. All dyestuffs may be said to vary in shade from red to yellow or from blue to yellow, and this variation from the standard type is designated by the letters B, G, R, etc.

Take, for instance, Methyl Violet, which varies in shade from 3 R to 6 B. The 3 R indicates a reddish shade nearly approaching Magenta, and 6 B indicates a bluish shade nearly approaching a product like Victoria Blue B. It follows from this that 3 R means a tint redder than 2 R, 3 B means a tint bluer than 2 B and 6 B denotes a still bluer shade than 3 B.

The letter G is generally the abbreviation for the German word "Gelb," which means yellow. The French word for yellow is "jaune." Consequently, French, Belgian and sometimes Swiss firms use the letter J where Germans use G. English and Americans employ for the same purpose the letter Y. 2 G means the same thing as if the letter G is repeated twice, and 3 G means the same as if it were repeated three times.

As to the use of the letter X and the word "extra," these two designations are by no means alike. The word "extra" is ordinarily used to indicate a quality superior to the regular type. This is sometimes shortened simply to the letter X.

More generally X indicates that the product in question is reduced 10 per cent below the standard type. XX in that case would mean that it is reduced 20 per cent below the standard type.

The mark W indicates that a dye is employed preferably for "wool," and HW refers to "half wool" or union fabrics.

The mark S indicates frequently a bisulfite compound, as in the case of Alizarin Blue S, SR and SW. Sometimes it denotes a sulfonic acid, as when used with Alizarin Red S, SA, and WS, or Fuchsine S, SS, SN and ST.—E. C. K.

BIBLIOGRAPHY OF RECENT LITERATURE ON FLOTATION.*

By D. A. LYON, O. C. RALSTON, F. B. LANEY, and R. S. LEWIS.

The object of this bibliography is to supplement previous bibliographies of flotation recently issued by the Bureau of Mines, covering articles issued in the technical press during the months of January to August, 1916.

In preparing this bibliography, articles in the following journals and periodicals published during September, 1916, have been abstracted:

Canadian Mining Institute bulletins.
Engineering and Mining Journal.
Metallurgical and Chemical Engineering.
Mining World.
Mining and Scientific Press.
Patent Office Gazette.
Proceedings of the American Institute of Mining Engineers.

Proceedings of the American Mining Congress.
Salt Lake Mining Review.

1. Adams, Maxwell. A new flotation oil from sage brush. *Min. and Eng. World*, vol. 45, Sept. 16, 1916, p. 490. Gives lists of some of its physical properties, together with method used in its extraction.

2. Belchie, George, and Neal, Roy O. Surface tension of oil-water emulsions—a flotation theory. *Min. and Eng. World*, vol. 45, Sept. 16, 1916, p. 487. Compares statements made by various authors regarding the value of oil flotation, and shows that uniform conclusions have not been reached. Discusses and gives tables of results of tests on surface tension carried on by the authors.

3. Burch, H. K. Concentration at Inspiration. *Eng. and Min. Jour.*, vol. 102, Sept. 2, 1916, p. 411; Sept. 9, 1916, p. 457. Description of Inspiration concentrator.

4. Clayton, Chas. Y. Flotation bubbles. *Met. and Chem. Eng.*, vol. 15, Sept. 15, 1916, p. 278. Shows and explains eight interesting photographs of flotation bubbles and bubble aggregates in the act of lifting particles of minerals to the surface.

5. Clevenger, G. H. A new source of flotation agents. *Am. Inst. Min. Eng. Bull.*, Sept., 1916, p. 1685. Discusses experimental work in the use of flotation methods and the various products resulting from destructive distillation of sagebrush.

6. Coghill, W. H. Molecular forces and flotation. *Min. and Sci. Press*, vol. 113, Sept. 2, 1916, pp. 341-349. Short illustrated article discussing and summarizing physical data upon which theory of flotation is based.

6. Cole, A. A. The production of flotation oils in Canada. *Can. Min. Inst. Bull.*, Sept., 1916, pp. 762-764. States that good flotation oils have been produced from red pine and spruce. The subject is being investigated by Canadian Government under direction of Minister of the Interior.

8. Cole, David. The advent of flotation in the Clifton-Morenci-District, Arizona. *Am. Inst. Min. Eng. Bull.*, Sept., 1916, p. 1611. Describe in detail experimental work which led to present flotation practice in Clifton-Morenci District.

9. Elmore, A. S. The invention, development, and introduction of the flotation process. *Min. and Sci. Press*, vol. 113, Sept. 23, 1916, pp. 449-455. Short history of flotation by one of the inventors of Elmore bulk oil process.

10. Engineering and Mining Journal. Automatic oil and acid feeder. Vol. 102, Sept. 9, 1916, p. 468. Describes U. S. patent 1,190,721, issued to Albert Campbell, July 11, 1916. The invention is a machine devised to feed regularly a given quantity of acid or oil into the ore stream.

11. —. Facilitating flotation. Vol. 102, Sept. 16, 1916, p. 520. Briefly discusses a few flotation oils.

12. —. Eberenz & Brown concentrator-flotation. Vol. 102, Sept. 23, 1916, p. 549. Describes apparatus for concentration of ore by gaseous flotation of mineral particles in liquid; U. S. patent 1,187,822, June 20, 1916.

13. —. Cyaniding of flotation concentrates. Vol. 102, Sept. 23, 1916, p. 561. Discusses application of process in Mexican plants, also the question whether contained oils will be detrimental to cyaniding.

14. Gahl, Rudolf. Notes on flotation. *Min. and Sci. Press*, vol. 113, Sept. 23, 1916, pp. 460-462. Extracts from paper on development of flotation at Inspiration presented at Tucson meeting of A. I. M. E., September, 1916.

15. —. Treating zinc-lead tailings at Midvale, Utah. Vol. 45, Sept. 2, 1916, p. 408. Describes method used for treating zinc-lead tailings from the plant of U. S. Smelting, Refining and Mining Co. Flotation machines used here are belt driven, instead of gear driven.

16. —. American Institute of Mining Engineers discusses flotation processes. Vol. 45, Sept. 30, 1916, pp. 577-578.

17. —. Oil-flotation process improved. Vol. 45, Sept. 30, 1916, p. 584. Frothing tendency of flotation oils can be increased by adding a certain percentage of resinates of an alkaline metal, such as soda, potash, or lime. Cites H. G. Varyan's patent, wherein inventor states that in practice he was able to obtain a superior flotation oil by mixing 50 per cent petro-

*Issued by U. S. Bureau of Mines.

leum, 15 per cent pine oil, and 35 per cent resinate of soda or resinate of ammonia.

18. Mining and Scientific Press. Agreement between Minerals Separation and the Inspiration-Anaconda companies. Vol. 113, Sept. 16, 1916, pp. 424-425. A verbatim copy of contract between these two companies as included in the evidence in the Minerals Separation versus Miami suit at Wilmington, Del., in 1915.

19. —. Flotation royalties. Vol. 113, Sept. 16, 1916, pp. 406-407. Editorial comments on contracts between Minerals Separation and the Anaconda and the Inspiration companies.

20. —. Comments on work of the Elmore brothers in flotation. Vol. 113, Sept. 23, 1916, pp. 445-446.

21. —. A new flotation oil. Vol. 113, Sept. 23, 1916, p. 467. Brief account of experiments at University of Nevada with oil from sage brush. The common sage brush (*Artemisia tridentata*) gives, upon destructive distillation, an excellent flotation oil.

22. Parmelee, H. C. Recent developments in zinc concentration practice in the Joplin District, Missouri. Met. and Chem. Eng., vol. 15, Sept. 15, 1916, p. 320. Discusses possibilities of flotation in Joplin district.

23. Pearce, J. A. Flotation tribulations. Min. and Sci. Press, vol. 113, Sept. 16, 1916, pp. 427-430. Discusses attempt to install flotation in the Argo mill in Colorado, its failure at first, followed by success.

24. Scott, W. A. Mining operations in Bingham Camp, Utah. Min. and Eng. World, vol. 45, Sept. 16, 1916, p. 492. States that as an addition to regular mill belonging to Utah Metal and Tunnel Co., they are building a flotation plant in a separate building to treat slimes from gravity concentrating mill. The plan is to pass slimes through Dorr classifiers and thickeners, after which it will pass to Pachuca mixers, where oils will be introduced before being treated by flotation machines, which consist of Callow cells, four roughers, and one cleaner. The new plant, it is thought, will be ready for operation late in September and it is expected to become a profitable adjunct.

25. Notes on Daly-West mill, Park City, Utah. Min. and Eng. World, vol. 45, Sept., 1916, p. 411. Gives comprehensive data on process used for treatment of ores.

PATENTS.

26. Bacon, Raymond F. Process for treating ores. U. S. patent 1,197,580, Sept. 12, 1916. Separation of non-sulphide minerals from associated gangue by subjecting them to action of hydrogen sulphide in presence of sulphur dioxide, whereby colloidal sulphur is formed and minerals are converted into sulphides, and ore recovered by flotation.

27. —. Concentration of ores. U. S. patent 1,197,590, Sept. 12, 1916. The method of separating metal constituents forming acid-soluble and acid-insoluble sulphides from each other and from associated

gangue by dissolving the soluble constituents with an acid, precipitating with hydrogen sulphide in the presence of and excess of acid and subjecting the resultant mixture to a flotation treatment.

28. Campbell, Albert. Oil and acid feeder. U. S. patent 1,190,721, July 11, 1916. Describes improvements in oil and acid feeders in flotation concentrators. Invention is directed to apparatus which will feed frothing agent to pulp in measured quantities. The object of the machine is that feed shall be constant and uniform irrespective of frothing agent in container or tank from which the same is fed to ore stream. A feeder is provided, the speed of which may be easily adjusted and controlled; one which is simple and light in construction and easy to operate.

29. Eberenz, G. B., and Brown, J. J. Ore-concentrator. U. S. patent 1,187,822, June 20, 1916. Describes apparatus for concentration of ore by gaseous flotation of mineral particles in liquid.

30. Mishler, Ralph T. Apparatus for separating oiled concentrates from the gangue of ores. U. S. patent 1,197,843, Sept. 12, 1916. A machine using both compressed air and mechanical agitation. A series of agitating blades are mounted upon a horizontal shaft.

NEW INSTALLATIONS AND OTHER NOTES OF INTEREST.

31. The Arizona Mine, Chaparral, Ariz., may install flotation in the new concentrating mill. Salt Lake Min. Rev., vol. 18, Sept. 15, 1916, p. 32.

32. Associated Consulting Engineers Co. of Salt Lake City state that the new flotation plant they constructed at the Lost Packer property, Loon Creek District, Idaho, is giving entire satisfaction. Salt Lake Min. Rev., vol. 18, Sept. 30, 1916, p. 34.

33. Big Four Exploration Co., Park City District, Utah, will install additional flotation equipment. Min. and Eng. World, vol. 45, Sept. 23, 1916, p. 559.

34. Black Cloud Mill, Salina, Colo., has recently been purchased by W. J. Blake and C. A. Newell, who are rebuilding it with flotation equipment. Salt Lake Min. Rev., vol. 18, Sept. 30, 1916, p. 35.

35. The Buffalo Mines Co., Cobalt, Ont., Can., on Sept. 5, put into operation the 600-ton flotation plant with Callow machines, which will treat tailings from dump of old mill as well as concentrates from mine. The previous system of treatment did not make anything like so close a recovery of silver as can be made by oil flotation. Re-treatment of tailings can be done profitably. Min. and Eng. World, vol. 45, Sept. 16, 1916, p. 523.

36. Butte & Superior Mining Co., Butte, Mont. Report filed in Federal court, Butte, Mont., shows that 45,874.287 tons of ore was treated in the company's oil flotation plant during July. Min. and Eng. World, vol. 45, Sept. 2, 1916, p. 432.

37. The C. & O. Co., Pinos Altos, New Mex., has taken over the Savanna properties and expects to install flotation process for treatment of Pinos Altos

ores. *Min. and Eng. World*, vol. 45, Sept. 16, 1916, p. 520.

38. The Consolidated Coppermines Co., Kimberly District, Nev., is to use Callow flotation process at the Giroux concentrator, Kimberly, Nev. Present plant is to be reconstructed. *Salt Lake Min. Rev.*, vol. 18, Sept. 30, 1916, p. 34.

39. —. Plant was recently inspected by J. M. Callow, the oil flotation expert, who advises installation of pneumatic flotation machines. *Min. and Eng. World*, vol. 45, Sept. 16, 1916, p. 520.

40. The 85 Mining Co., Lordsburg District, New Mexico, it is believed, will soon erect a flotation plant at its property. A test mill has been established by the company at Texas School of Mines, Fort Bliss, Texas. J. W. Crowdus, in charge, is making complete tests of flotation in hopes of finding proper method for treating the ore. *Min. and Eng. World*, vol. 45, Sept. 16, 1916, p. 520.

41. The Florence-Goldfield Co., Goldfield, Nev. The flotation plant is treating more than 200 tons a day. A new flotation machine, the Jones-Belmont, is giving satisfaction. Product now going to mill averages \$5.00 per ton, but a higher grade ore will soon be treated. *Min. and Eng. World*, vol. 45, Sept. 2, 1916, p. 433.

42. The Florida group, near Lida, Nev., will possibly have a flotation plant of large capacity, as plans for one are being matured, according to the Goldfield News. *Salt Lake Min. Rev.*, vol. 18, Sept. 15, 1916, p. 32.

43. The Forbestown Consolidated Co., Forbestown, Cal., after a series of experiments extending over 18 months, has demonstrated efficiency of flotation process. It is stated that a 98 per cent extraction has been obtained. *Min. and Eng. World*, vol. 45, Sept. 23, 1916, p. 553.

44. David Gemmill, of the Randolph Reduction Works, Crown King, Ariz., has solved a treatment by flotation for base ores of that section and is utilizing it with success.

Gemmill's improvement to oil-flotation process, more than any other single factor, has been instrumental in bringing to life in the Bradshaw mountains, Crown King District, Ariz., many of the old-time producers. *Min. and Eng. World*, vol. 45, Sept. 16, 1916, p. 514.

45. The Gillard Tungsten Mining & Leasing Co., Cripple Creek, Colo., is preparing plans for a flotation and cyanide plant for treating low-grade custom ores. *Min. and Eng. World*, Sept. 30, 1916, p. 595.

46. The 1,000-ton flotation unit was, on August 21, at full capacity. The management expects after a few weeks to maintain a daily output of 1,050 tons and to better gold extraction, which now approximates 92 per cent. *Min. and Eng. World*, vol. 45, Sept. 2, 1916, p. 433.

47. —. Flotation mill is now treating 1,000 tons of ore daily, and handling some ore of excellent

grade from newly opened lower workings. *Min. and Eng. World*, vol. 45, Sept. 9, 1916, p. 473.

48. —. Pending installation of additional thickeners and filters in the mill, flotation has been temporarily discontinued. The process, it is stated, has proven a success, and it is expected that the plant will resume within 60 to 90 days. Meanwhile the company will revert to cyanide process. *Min. and Eng. World*, vol. 45, Sept. 23, 1916, p. 557.

49. Owing to lack of equipment to settle and filter flotation concentrates, and on account of changes in ore, the company has temporarily abandoned flotation. *Min. and Eng. World*, vol. 45, Sept. 30, 1916, p. 588.

50. Goldfield Great Bend Mining Co., Goldfield, Nev., is experimenting with flotation and the process will probably be installed. *Salt Lake Min. Rev.*, Sept. 15, 1916, p. 32.

51. The Keystone Consolidated Mining Co., Chloride, Ariz., has let a contract for construction of a 100-ton Fields flotation plant. *Salt Lake Min. Rev.*, vol. 18, Sept. 30, 1916, p. 33.

52. Lost Packer Mining Company's flotation process recently installed at its mill, Bonanza, Idaho, is stated to have solved problem of working low grade ores of that property. *Salt Lake Min. Rev.*, vol. 18, Sept. 30, p. 35.

53. The Nipissing Mining Co., Cobalt, Ont., has been experimenting with Callow flotation process with good results. *Salt Lake Min. Rev.*, vol. 18, Sept. 15, 1916, p. 33.

54. The Shattuck Arizona Copper Co., Bisbee, Ariz., is experimenting with flotation for its low-grade silicious gold-silver-lead ores. *Salt Lake Min. Rev.*, vol. 18, Sept. 15, 1916, p. 32.

55. C. F. Sherwood, formerly metallurgist for Butte-Superior Mining Co., and later of Butte-Duluth Mines, who worked out process for sulphidizing and treating by flotation the carbonate mill tailings of the Prince Co., at Bullionville, Nev., has opened an office and metallurgical research laboratory at Salt Lake, Utah. *Min. and Eng. World*, vol. 45, Sept. 9, 1916, p. 465.

56. Silver King Coalition Mines Co. is making a better saving of values since installation of flotation process. *Salt Lake Min. Rev.*, vol. 18, Sept. 30, 1916, p. 30.

57. The Southwestern Engineering Co., Los Angeles, Cal., has issued an article entitled "Flotation Concentration Testing" in its Bull. No. 2, p. 4, which gives briefly the nature of flotation tests it makes. These tests are divided into three classes, those on 10 to 25 pounds of ore, 100 pounds, and 150 pounds. The test for each class and the charge for it are given. *Min. and Eng. World*, vol. 426, Sept. 2, 1916, p. 426.

58. Utah Metal & Tunnel Co., Bingham, Utah, has announced that flotation process will be completed and in operation immediately at their mill and should result in saving not less than \$6,000 a month. *Min. and Eng. World*, vol. 45, Sept. 30, 1916, p. 601.

59. Walker Copper Mine, Portola, Cal., which has been acquired by the International Smelting & Refining Co., has recently completed its 100-ton daily capacity flotation plant. *Min. and Eng. World*, vol. 45, Sept. 2, 1916, p. 428.

60. The Weringer Mines Co., Woody, Cal., is constructing a flotation plant of 100 tons capacity at its copper mine. *Min. and Eng. World*, vol. 45, Sept. 9, 1916, p. 469.

61. —. A Hardinge mill, Dorr classifier, Oliver filter, and several flotation machines have been ordered for its 100-ton plant. *Min. and Eng. World*, vol. 45, Sept. 23, 1916, p. 553.

MANUFACTURERS' SPECIFICATIONS FOR PURCHASE OF GASOLINE.

In direct response to the request of the General Supply Committee of the executive departments of the Federal Government in the District of Columbia for specifications to govern the purchase of gasoline in the District, the Bureau of Mines, Department of the Interior, has prepared tentative specifications and has sent copies of them to the refiners, automobile engineers, jobbers, and other men prominent in the industry, with the request that the draft be criticized in order that when the specifications are finally issued they will be fair alike to the refiner and consumer. It is hoped that as a result of the consensus of opinion of all the interested parties specifications can be prepared that will be of value not only to the Federal Government in the District of Columbia, but to the entire public using gasoline for fuel purposes.

There is at the present time a considerable difference as to the grading of gasolines. The bureau has attempted to grade gasolines, bearing in mind the principal motor purposes for which gasoline is used.

In the tentative specifications, the specific gravity test has been eliminated, as it is generally considered that specific gravity alone means little and is entirely inadequate, since it may give a high rating to a poor gasoline and a low rating to a good one. At present, the general tendency is to either specify tests which are unreliable, or else make requirements which are unreasonably severe. Many buyers believe that only straight refinery gasoline, and not casinghead gasoline and cracked products, are desirable, and the test they require discriminates against a large portion of our market supply of gasoline.

The basic property which determines the grade and usefulness of a gasoline is volatility. It is not, however, a property whose influence may be stated concisely and in a few words. It is of course advantageous to have motor fuel vaporize easily. It is of course obvious that gasoline is not gasoline if it can not be converted into an explosive gaseous mixture under conditions existing in the engine. These simple considerations would lead to the conclusion that the desirable product is one having a fairly high initial boil-

ing point and a low end point. Here again, however, it is necessary to take account of further considerations which complicate the matter. The first is that a gasoline of narrow and selected boiling range is bound to be exceedingly expensive. In addition it is not an unmixed advantage to have such a product. A high initial boiling point tends to make the engine in which such a product is used difficult to start in cold weather. It is also a question as to whether or not the low end point is an unmixed advantage. Some of the refiners of so-called blended products claim that the presence of the heavier naphthas causes the explosion in the engine cylinder to take place more slowly than in the case of lighter gasoline. The piston head is drawn through the same distance and the same power is developed, but the force is applied with a gradual push rather than with explosive violence. It is claimed that this sort of action lessens the strain on the engine and actually tends toward greater power production.

These are claims for which as yet no conclusive experimental proof seems available. They seem, however, entirely plausible and are more than likely to receive credence because such products are bound to be used on account of cheapness.

In summing up the desirability of various degrees of volatility, it appears that it is desirable to have a certain percentage of fairly low-boiling constituents so that engines may start readily, but undesirable that such constituents should be present in too large proportion, on account of the resulting increased possibility of loss through evaporation and of accidental ignition and explosion. A reasonably low end point is desirable in order to insure complete vaporization, but it makes the gasoline expensive. In addition, if it is possible to utilize high end point gasolines efficiently, it seems conceivably possible to develop maximum power with less strain on the engine. For these reasons, the end point should be as high as is possible, without exceeding a limit set by the ability of the engine to atomize and vaporize the gasoline properly. It is, of course, impossible to set limits which will meet all needs, but figures have been chosen which general use seems to indicate as most practical.

The analytical methods used for the testing of gasoline are of fairly recent development, but no adequate description of them appears to be available. Some of the tests employed are not standardized, and there are substantial differences in the methods by which they are conducted in various laboratories. There seems also to be a lack of knowledge regarding the practical interpretation of results obtained by analysis. The tendency is to overemphasize some particular figure. Formerly specific gravity was considered the complete index of the qualities of gasoline. At present a similar overemphasis is placed on the so-called "end point" of the Engler distillation. One of the chief objects of the proposed gasoline specifications is to indicate rationally methods of interpreting the analytical results.

At the present time there are sold in the market several grades of gasoline, these generally being classified according to their specific gravity, although the distinctive quality is that of volatility. The gasolines with low specific gravity and generally with low boiling range selling for the highest prices. Heavier grades are cheaper, and if properly used are capable of developing more power per unit volume than are the lighter gasolines. The Bureau of Mines has considered it advisable to divide gasoline into three classes, to be designated according to the maximum temperature limit (in degrees Centigrade) below which which 90 or 95 per cent by volume must distill. Keeping in mind that the high-grade gasoline is to be used for special purposes, such as for aeroplanes, etc., and should include products of the type now sold in the Eastern market as of 70° Baumé or over. The middle grade is to be used for automobiles of a design of, say, two years ago, and is represented by the type of gasoline now sold in the Eastern market which ranges from 65 to 70° Baumé. The third grade, represented by the gasolines now sold in the Eastern market as around 60° Baumé gravity which is being used satisfactorily in up-to-date automobile engines. It is, of course, realized that the automobile engine has been improved so that it can use a heavier grade of fuel than was possible a few years ago.

The essentially desirable properties of gasoline may be stated briefly as follows:

(1) Neither the gasoline nor its products of combustion should have a strong or markedly disagreeable odor, this being objectionable to users of automobiles.

(2) The gasoline should be free from matter which is not hydrocarbon, such as water, sediment, acid, etc.

(3) The gasoline should be free from bodies which either originally or after combustion attack the metal composing the engine. Unremoved acid in refining, and excessive sulphur content, fall under this head.

(4) The gasoline should not contain excessive percentages of unsaturated or aromatic hydrocarbons, since some evidence is at hand which indicates that there may be limits in the ability of motors, as at present constructed and adjusted, to utilize these products.

(5) The gasoline should not contain too high a percentage of very volatile products which tend toward high evaporation losses and excessive danger in handling and storage.

(6) The gasoline should not contain any considerable percentages of heavy or non-volatile constituents which prevent the atomization into engine cylinders of a mixture which can be completely burned.

The above stated requirements are simple in principle and are almost axiomatic. The only problem is to fix limits, defined by experimental practice, which shall satisfy the desirable conditions.

There are at present on the market types of gasolines produced by several general refining methods. These may be classified as follows:

1. "Straight" refinery gasoline.
2. Blended casinghead gasoline.
3. Cracked and blended gasoline.

"Straight" Refinery Gasolines.—"Straight" refinery gasolines are produced by methods which vary somewhat in different parts of the country, but are in general similar. Crude oil is distilled in a fire still and a cut made when the gravity of the product reaches some predetermined mark. The so-called crude naphtha or benzine is acid refined and then steam-distilled. In some cases several products of different ranges of volatility are produced, in others the steam distillation simply effects a separation from less volatile bottoms which go into the burning oil stock.

"Straight" refinery gasolines are characterized by low content of unsaturated and aromatic hydrocarbons, and by a distillation range which is free from marked irregularities.

Blended Casinghead Gasolines.—A product which has come on the market during the last few years is so-called casinghead gasoline which is produced from "wet" natural gas by processes of compression or absorption. "Straight" casinghead gasoline is too volatile for general use and before being put on the market is blended with a sufficient proportion of heavy naphtha to produce a mixture which is both safe for use and moderately cheap. Blended casinghead gasolines are generally characterized by a volatility range showing considerable percentages of constituents boiling at both low and high temperature, but a deficiency of intermediate products. In some cases, however, the blending is done in such a manner that it is difficult to detect the natural-gas gasoline. This is when it is used in moderately small proportion to lighten and to make more volatile gasoline which has a boiling range approximately the same as that satisfactory for motor purposes.

As far as chemical properties are concerned, casinghead gasoline seems to be identical with the "straight" refinery product. The characteristic properties are, therefore, wholly due to the details of blending.

Cracked or Synthetic Gasoline.—One of the important factors in the present gasoline market is the production of cracked or synthetic gasolines. These are being marketed in enormous quantities, largely if not altogether, in the form of blends with "straight" refinery and casinghead gasoline.

Cracked gasolines are similar in physical properties to "straight" refinery products, but are different chemically in that they contain varying percentages of unsaturated and aromatic constituents. It has been demonstrated that these constituents do not decrease the value of a gasoline, if they are not present in too great proportion. It is still an open question whether or not motor fuel containing very high percentages of

unsaturated compounds can be utilized in the same way as the "straight" refinery products.

Attention is also called to the fact that refiners are today marketing gasoline containing considerable percentages of unsaturated compound, and these products are being satisfactorily used by the public.

WAR TIME USES OF FOREST PRODUCTS.*

By A. W. SCHARGER.†

One of the mysteries of the present war is the source from which Germany obtains the nitrocellulose necessary in the manufacture of smokeless powder, ordinarily made from cotton. A well defined belief exists in England that at least part of the nitrocellulose needed by German powder factories is being made from wood; and if this is true it furnishes another instance of the surprising dependence upon wood, in one form or another, on the part of the fighting nations. The actual extent to which forest products are put to use in time of war, both for military purposes and for supplying the nation with some of the things it needs to carry on its daily life, is not generally recognized.

Conditions of course have changed vastly since the day when Pepys offered up thanks in his diary for "the very good news of four New England ships come home safe to Falmouth with masts for the King; which is a blessing mighty unexpected, and without which we must have failed the next year. But God be praised for this much good fortune, and send us the continuance of His favor in other things." Wood has ceased to be a large factor in ship building. Sea battles of today are fought by all-steel dreadnoughts; even the wooden backing of the armor plate is giving way to other material. Wooden decks alone remain to link the old fighting ship with the new. But warfare on land has developed in a way to give timber an importance in field operations it never had before, while the vast number of accessories needed for the smooth running of the modern fighting machine, from ammunition to absorbent cotton, have led to an extraordinary demand for certain forest products, and have even brought about new uses for wood born of necessity and unheard of a few years ago.

For one thing, there is the matter of explosives. Ordinary black powders contain about seventy-five parts saltpeter, ten parts sulphur, and fifteen parts charcoal. The charcoal employed must possess special properties, and is made largely from dogwood, willow and alder. In spite of the advent of smokeless powder, enormous quantities of black powder are still used. It is employed in shrapnel, for which only a moderately powerful explosive is required to drive the bullets. Besides, the smoke produced when the

shell explodes is an actual advantage in enabling the gunners to determine the correct range.

Black powder is also used to fill the rings of the time fuses with which shrapnel shells are equipped, for which purposes no satisfactory substitute has yet been found. Furthermore, it is used in most armor-piercing shells, which should attain great penetration before they go off, and for which the majority of high explosives would be unsuitable because of their explosiveness on contact. Another product of the forest, rosin, is employed for filling the spaces between bullets in shrapnel, so that on explosion the missiles will be evenly distributed in all directions. Its brittleness and at the same time its hardness, together with its low melting point, fit it admirably for the purpose.

The period since the beginning of the war has witnessed a great amount of discussion in England as to whether Germany is actually employing wood from which to make the nitrocellulose for its smokeless explosives. When, after a long delay, England declared cotton contraband of war, it was maintained by many that this would not inconvenience Germany greatly, since it already was making explosives from wood cellulose. During the discussions that followed it was proposed to destroy the forests of Germany by a giant fleet of aeroplanes armed with bombs; however, as one English editor naively remarks: "This would scarcely be feasible since about one-third of Germany is forested."

As a matter of fact, little or no reliable information exists in regard to Germany's use of wood for nitrocellulose, and expert opinion in England differs widely about the matter. Sir William Ramsay believed that such explosives were being made, and Walter F. Reid, who introduced the important gelatinization process in the manufacture of smokeless powder, is emphatic that a nitrocellulose can be made from woodpulp that is equal in every respect to that made from cotton. On the other hand, Clayton Beadle, whose opinion is entitled to great respect, holds that the difficulties attending proper purification of the wood cellulose previous to nitrification are all but insurmountable.

However this may be, records published by German scientists before the war show that a high explosive can be manufactured from wood cellulose, though at that time its stability was questionable, and while it required forty years of experiment to render gun-cotton stable anything like the same time might not be necessary in the case of wood cellulose, for the experience with gun cotton should facilitate solution of the present problem. It is highly probable that the chemical difficulties already have been overcome.

In this connection it is an interesting fact that the first successful smokeless powder was made from wood about 1865. This powder, invented by Schultze, consists of a mixture of saltpeter and nitrated purified wood. While inferior to guncotton in ballistic power,

*From the American Lumberman.

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it still retains high favor among sportsmen. Various other explosives, known as "white powder," "yellow shooting powder," and "Bautzen blasting powder," contain nitrated lignocellulose.

Aside from munitions, wood is serving many useful purposes in the war. Millions of gunstocks are made from American walnut, which is the best wood yet found for the part. A new rifle, it has been estimated, is required monthly for every man at the front. In the modern infantry weapon the wood stock is prolonged to the end of the barrel, which means just so much more wood needed in its manufacture. So great has been the demand by gun makers for seasoned walnut that it has often been necessary to use birch and other woods as substitutes.

With characteristic foresight the Germans brought portable sawmills with them into France and have utilized their enemy's forests to supply their need for timber at the front, while reserving their own forests for home demand. The development of trench warfare, when vast armies of men dig themselves in on fronts hundreds of miles long, calls for an amount of timber for trench walls, floors and braces that it is difficult to estimate. Millions of feet of lumber are required also for temporary buildings behind the fighting line and for housing noncombatants made homeless by the fortunes of war. Still more goes into bridges, wharves and the like. High explosives have made it possible for a retreating army to destroy stone and steel structures behind them in short order, and such structures the pursuing army must have the means of quickly replacing. Wood is, in most cases, the only material that will answer the purpose. And it served the German army in good stead during the pursuit of the Russian army through Poland.

Turning from the materials needed for actual fighting to the less important ones required for proper care of the wounded we find Germany, fully prepared for England's embargo, making a soft, absorbent surgical cotton from wood cellulose. Two factories in Sweden also are making this substitute. Slings are made from tough crepe paper, and splints from fiber boards.

Wood is also contributing to the personal comfort of the men at the front. Russian soldiers are wearing paper shirts made in Japan, where such clothing has been in use for many years. The chief raw material for the manufacture of paper is, of course, woodpulp. Paper clothing is warm and cheap, and special waterproofing processes are overcoming its tendency to tear when wet. It may be discarded when soiled, an advantage to the soldier from the standpoint of hygiene. The Germans and Austrians, mainly the poorer classes of the civilian populations, use paper vests, socks and handkerchiefs. Blankets and coats are padded with cellulose wadding. So many paper articles, in fact, are produced for the comfort of the people of Germany and Austria as to lead the Socialist or the

Forwaerts to declare, "To be without wood is almost as bad as being without bread."

To insure the presence of every factor that tends to eventual success a country at war needs to maintain its economic conditions as nearly as possible at their normal level. Products of the forest play an important part in many peaceful industries which must be kept going in war time.

Methyl alcohol, the other product besides acetic acid obtained from the destructive distillation of hardwoods, has a multitude of uses. For one thing it is essential in the manufacture of many medical preparations. For another, it is employed in the making of aniline dyes, the scarcity of which is being felt throughout the world. It is the source, also, of formaldehyde, one of the safest and most efficient antiseptics known, for the manufacture of which large quantities of wood alcohol are exported to Europe.

The longleaf pine forests of the South furnish 90 per cent of the world's supply of turpentine and rosin. In normal times turpentine is used mainly as a solvent in the arts. It is entirely possible, however, should the need arise, to make from turpentine a synthetic camphor as good for practical purposes as the natural product. In the event of the blockade of the Pacific coast this should be the means of preserving our celluloid industry, which now consumes the greater part of the 5,000,000 pounds of Japanese camphor imported annually.

Rosin, the use of which in shrapnel has already been mentioned, is employed mainly in the manufacture of cheap soaps and as a size for paper. So acute has become the scarcity of rosin in Germany that the Prussian Minister of Agriculture has suggested such measures for increasing the supply within the Empire as distilling resinous wood and collecting the oleoresin which exudes from trees peeled by deer. Prices being paid for rosin by the Central Powers are almost fabulous. Curiously enough, a substitute for paper size recently proposed by a German scientist has wood tar as its base.

In connection with the use of rosin as size for paper should be mentioned the fact that in time of war, the demand on the forests for print paper deserves serious consideration. Of the 6,000 newspapers and periodicals in Germany and the 3,000 in Austria at the beginning of the war it is estimated that about 1,100 of the German and 900 of the Austrian have since suspended publication either through inability to obtain paper or because of its prohibitive price. Germany has always imported large quantities of pulpwood from Sweden and Russia so that cessation of importation of Russian pulpwood and American rosin is a partial cause of the trouble. On the other hand, German war literature has been augmented by some 7,000 books and pamphlets since the beginning of hostilities; and it is the invariable rule in all countries that the demand for newspapers and periodicals of all kinds increases enormously in a time of national crisis.

The total daily circulation of French newspapers before the war, for example, amounted to approximately 7,000,000 copies. The circulation has now increased to 15,000,000 daily in spite of the suspension of a number of journals. The bulk of print papers is made from spruce and balsam fir. Experiments at the Madison laboratory of the Forest Service have shown, however, that satisfactory newsprint paper can be made from about seven or eight other American woods, which places the United States in a position of preparedness, at least so far as the production of paper is concerned.*

The binder twine, used everywhere in the United States in connection with harvesting our crops, is at present made from sisal imported from Central America and Mexico. As a result of the disturbed conditions in Mexico, American twine manufacturers are seriously embarrassed for raw material. A substitute has been sought in paper twine and experiments in this direction are under way.

Strong cordage, ropes, burlap and similar articles can be made from paper, and, in fact, are being made from it. Our common burlap and coarse bags are ordinarily made from imported jute. Shortly after war was declared the price of burlap bags increased so greatly that one large grain dealer seriously considered taking the profit to be derived from the sale of his reserve stock of bags and going out of business. In the case of a war of our own, the United States should be in a position, through its enormous supplies of wood fiber, to meet all or at least the greater part of its needs for the twine necessary to harvest its crops and for substitutes for burlap bags and hemp ropes.

The American public, perhaps unaware, has long been accustomed to articles of clothing made from wood under the terms "fiber silk" and "artificial silk." The viscose process transforms woodpulp into a strong, durable, lustrous thread that may be woven into any desired fabric; accordingly the morning newspaper and handsome cravat may have a common origin.

Finally, should the South ever be invaded and its cotton crops seized, a happening which military and naval authorities regard as not at all unlikely in case of war with a strong power, the cellulose from our forests would have to serve us not alone for explosives, but for textiles as well. Thus in more ways than in the production of lumber the forest may serve a nation called upon to meet the conditions of modern warfare, and for that matter, too, of commercial progress in time of peace. Nor is it beyond the bounds of possibility that the investigations and experiments which are being carried on at the Government's Forest Products Laboratory and elsewhere may find still other uses for wood that will add just so much more to the importance of the forest in our national life.

THE NITRATION OF TOLUENE.*

By E. J. HOFFMAN.

This paper is the result of experiments made in the Bureau of Mines on the preparation of trinitrotoluene from toluene obtained in the manufacture of water gas. There seems to be a rather prevalent view that so-called water-gas toluene is unsuitable for the manufacture of trinitrotoluene, because of the toluene containing hydrocarbons of the aliphatic series whose removal cannot be effected by the usual methods of purification. It was in anticipation of such difficulty that the present investigation was undertaken.

The investigation early showed that if the sample of water-gas toluene under investigation contained any aliphatic hydrocarbons they were present in negligible quantity so far as affecting nitration. Consequently, the investigation became a more general one, embracing the nitration of any good grade of toluene, and it was continued with a view not only of ascertaining the conditions under which the best yield of trinitrotoluene could be obtained from the sample in hand, but also of developing a method that might be capable of satisfactory industrial application to the nitration of any toluene of approximately the same degree of purity.

Ample justification for such an investigation is to be found in the incompleteness of published details with respect to methods already successfully applied in the industries. Although much valuable information was available in the literature on the nitration of toluene, the author was unable to select any method or combination of methods described that could be said to cover the whole problem in hand; nor were the data available sufficient to determine the relative merits of different procedures with respect to quantity and quality of yield of trinitrotoluene.

TECHNICAL METHODS FOR MANUFACTURE OF TRINITROTOLUENE.

Early Processes.—A trinitrotoluene having a melting point of 82° C. was prepared in 1863 by Wilbrand (5) by the action of fuming nitric and sulphuric acids on toluene. By the further nitration of dinitrotoluene, Beilstein and Kuhlberg (9), in 1870, and Tiemann (10), in 1870, obtained similar products. In 1882 Hepp (15), by the action of very concentrated acids on paranitrotoluene and 2-4 dinitrotoluene, obtained a considerable quantity of α trinitrotoluene. Metanitrotoluene yielded by the same treatment β and γ trinitrotoluene.

Häussermann's Method.—Häussermann (26), in 1891, described a technical method for the manufacture of trinitrotoluene (TNT¹) which avoids the highly concentrated acids of Hepp. One hundred parts of paranitrotoluene was treated with a mixture

*From a technical paper issued by the U. S. Bureau of Mines.
¹For the sake of brevity in the following pages the abbreviation "TNT" is used for "trinitrotoluene." Similarly "DNT" and "MNT" stand for "dinitrotoluene" and "mononitrotoluene."

of 75 parts of 91 and 92 per cent nitric acid with 150 parts of 95 to 96 per cent sulphuric acid. During the addition of the nitrating acids the temperature was maintained at 60° to 65° C., after which the mixture was further heated at 80° to 85° C. for one-half hour. The yield of DNT melting at 69.5° C. was approximately 130 parts. The latter was slightly heated, dissolved in 4 parts of 95 to 96 per cent sulphuric acid, and treated with 1.5 parts of 90 to 92 per cent nitric acid, after which the temperature was kept at 90° to 95° for 4 to 5 hours. The yield of TNT (melting point 70° C.) was 105 parts from 100 parts of DNT, by recrystallization a product having a melting point of 81.5° C. was obtained.

Method of Vasquez.—Vasquez, 1911, described a method for the manufacture of TNT from toluene in three stages, and gave details of apparatus and procedure in manufacture and refining. According to this method the spent acids (90 liters) from the preparation of DNT are fortified with the required nitric acid and added to an equal weight of toluene, with constant stirring and with cooling, to prevent a rise of temperature above 30° C. After standing 6 hours the resultant MNT is separated.

The spent acid is regenerated by the use of sulphur trioxide and mixed with a quantity of nitric acid equal in weight to the MNT formed. The mixed acid is added as above to the MNT at a temperature of 90° C. After 6 hours the product is cooled to -2° C., and the spent acid is drawn off from the DNT.

For the third stage of nitration stronger acids are added to the molten DNT, raising the temperature to 92° C. After 20 hours the mixture is transferred to another vessel, and after 4 to 5 days the separated solid is washed with water and alkali, then refined by being washed with acetone and soda, and finally crystallized from alcohol.

Langenscheidt's Method.—A method devised by Langenscheidt to obviate the necessity of separating the DNT from the spent acid after the conversion of orthonitrotoluene into DNT is as follows: Five hundred kilograms of orthonitrotoluene is dissolved in 1,400 kilograms of 100 per cent sulphuric acid and warmed to 60° to 70° C. The mixed acid consisting of 700 kilograms of 100 per cent sulphuric acid and an equal weight of 48° B. (94.09 per cent) acid is introduced in a thin unbroken stream. In the beginning the reaction is violent, and much cooling is required; as the nitration proceeds the heat evolved decreases. A fall in temperature indicates that the orthonitrotoluene has gone over into the second stage of nitration. All the mixed acid is gradually introduced, and the whole is slowly warmed up again until a further reaction takes place—the nitration of DNT to TNT. The heat evolved in this stage of the nitration is not so great as in the first stage. If means of cooling the liquid are not used, the temperature usually rises to 120° to 130° C. As soon as the temperature begins to

fall the contents of the nitrating vessel are brought to 150° C., and this temperature, or just as well, a temperature of 120° to 130° C., is maintained for about one hour. When the reaction mixture has cooled to 100° C., about 200 liters of water is added to increase the yield.

Langenscheidt's method for manufacturing TNT from DNT is as follows: Five hundred kilograms of DNT is placed in the apparatus and melted; the mixed acid consisting of 1,125 kilograms of oleum (20 per cent) and 305 kilograms of nitric acid (48° B.) is slowly added at 70° to 75° C. When the addition of acid has been completed, the contents of the apparatus are slowly and carefully warmed. The reaction begins at 90° to 100° C., and a temperature of 130° C. is reached, which is maintained for one hour, after which the products are cooled to 100° C. and treated as above with water.

The resultant TNT separated cold by the method here indicated, or in the liquid condition, is forced into lead wash tanks containing water at 40° to 45° C., and washed with steam till neutral. By crystallization from a mixture of 9 parts of alcohol and 1 part of benzene a product is obtained that melts at 81° to 82° C. and solidifies at 80.3° to 80.4° C.

Method of Vennin and Chesneau.—The following method of Vennin and Chesneau provides for the direct nitration of toluene to TNT in one operation: Twenty kilograms of toluene is added slowly to a mixture of 86 kilograms of 91 to 92 per cent nitric acid, 450 kilograms of 93 to 94 per cent sulphuric acid, and 25 kilograms of oleum (60 per cent sulphur trioxide) at 40° C. The mixture is then heated 2 hours at 80° to 85° C. and 3 hours at 100° to 105° C. After the mixture has cooled the spent acids are drawn off, and the TNT is crystallized from hot sulphuric acid and washed with hot water. The product thus obtained melts at 77° to 70° C. By washing with 95 per cent alcohol, or alcohol containing 10 per cent benzene, a product is obtained that melts at 81° C. The yield is given as 150 per cent referred to the toluene used.

Importance of available Alcohol.—As prepared by the methods described above the TNT of desired purity is obtained by crystallization from alcohol. If the necessary alcohol is available at a reasonable cost this procedure presents no difficulties, but if, for economic reasons, alcohol can not be used it is necessary to proceed in such a way that crystallization of the water-washed product is avoided. The direct nitration of toluene to dinitrotoluene yields mainly the 2-4 DNT; but the product contains also 7 to 10 per cent of an orange-yellow oil known as "drip oil" (German "Tropföl" or "Binitropföl"), which investigation (11, 12, 16, 17, 19, 28, 30, 50, 53) has shown to consist of traces of orthonitrotoluene, about equal parts of meta and para MNT, the 2-4, 2-5, 2-6 and 3-4 DNT'S, 2-4-6 TNT, and either 2-3-5 or 2-3-6 TNT. In Germany

this liquid affords a valuable and economical starting point in the manufacture of TNT. In Italy, however, by starting with a DNT product having a melting point of 63° to 66° C., a TNT is prepared that without crystallization from alcohol melts at a temperature only 1° to 1.5° lower than that required for the pure TNT.

Giua's Method.—Giua recently describes a method for thus preparing a high grade of TNT. Pure toluene, in a special nitration apparatus provided with a stirring device to keep the liquid constantly agitated, is nitrated with a mixture of nitric and sulphuric acids containing 18 to 22 per cent nitric acid and 15 to 20 per cent water. To assure a satisfactory product, 1.5 to 1.8 times the theoretical amount of nitric acids must be used. The temperature of reaction must not rise above 110° to 120° C. By the use of the centrifuge or other mechanical means the drip oil formed can be removed sufficiently from the solid DNT so that by washing well with water a product is obtained that melts at 63° to 66° C.

Subsequent nitration of this product is accomplished by treatment with anhydrous acid containing 18 to 25 per cent nitric acid, the ratio of toluene to nitrating acid being 1 to 4 or 1 to 5. The reaction begins at 60° to 65° C.; the temperature is regulated by cooling means so that it does not exceed 118° to 122°. By treatment with the nitrating acid mentioned in the ratio of 1 to 2 the red oil removed from the solid DNT yields at 66° product.

Method of Escalles.—Escalles has described in detail apparatus and methods for preparing the various nitrotoluenes, the following abstract being taken from his description.

1. *Mononitrotoluene.*—The toluene (200 kilograms) is introduced into the proper nitrating vessel, provided with a cooling and a stirring apparatus. The nitrating acids, 350 kilograms of 66° B. sulphuric acid (specific gravity 1.84) and 225 kilograms of 44.1° B. nitric acid (specific gravity 1.41), are added over a period of 8 hours. The temperature attained in 1 hour (60° C.) must not be exceeded. After introduction of all the acid the operation is continued 2 hours longer, after which the mixture is allowed to stand overnight. The spent acid is used over again for the preparation of the next lot of MNT, after addition to it of 150 kilograms of 44.1° B. nitric acid. If the mononitrotoluene is desired for other purposes, isomers may be separated and purified. Otherwise this crude mixture is further nitrated to DNT.

2. *Dinitrotoluene.*—To the crude MNT prepared in the manner described is added a stronger acid mixture, 675 kilograms of 66° B. sulphuric acid, and 225 kilograms of 46.8° B. nitric acid (specific gravity 1.445), over a period of 6 hours. In about 1.5 hours the temperature normally reaches 115° C. The operation is completed in a total time of 9 hours, when the DNT is separated hot from the acids and emptied into

boiling water. If the course of the reaction has been defective the oil ("Binitropfol") thus formed is allowed to drain off. Otherwise the total product is crushed and treated with water. Any impure product present collects on the surface of the water and can be removed. In operations 1 and 2, 200 kilograms of toluene yields 350 to 360 kilograms of dry DNT, or 90 to 93 per cent of that required by theory.

3. By the use of still stronger acids the pure DNT may be readily converted into TNT.

The methods of Häussermann, Vasquez and Langenscheidt are given in detail.

DESCRIPTION OF NITRATION EXPERIMENTS.

FOUR METHODS OF PREPARING TRINITROTOLUENE.

The methods outlined above for the preparation of trinitrotoluene involve all of the four possible procedures for converting toluene into the desired product, as follows:

1. A one-stage method, comprising the direct nitration of toluene to trinitrotoluene in one operation.

2. A two-stage method, comprising: (a) The conversion of toluene into dinitrotoluene; and (b) the further nitration of the dinitrotoluene to trinitrotoluene.

3. A two-stage method, comprising (a) the preparation of mononitrotoluene; and (b) the conversion of mononitrotoluene into trinitrotoluene.

4. A three-stage method, comprising: (a) The preparation of mononitrotoluene; (b) the conversion of mononitrotoluene into dinitrotoluene; (c) the further nitration of dinitrotoluene to trinitrotoluene.

Method 1.—A modification of the method described by Vennin and Chesneau was employed by the author of this paper in the nitration of a laboratory sample of toluene boiling at 110.5° C. Because of the low yield of TNT (138 grams—melting point 79.5° to 81° C.—Per 100 grams of toluene) and the large amount of acid required, this method was abandoned as uneconomical.

Method 2.—No effort was made to utilize method 2 on account of the recognized difficulties due to the formation of liquid products ("drip oil") along with the solid dinitrotoluenes. Two preliminary experiments gave very unsatisfactory results.

Methods 3 and 4.—Probably method 4 is the one most commonly used by manufacturers of TNT, at least, in this country, and in addition to any other economical advantages it may possess, it is much the most satisfactory if the manufacturer desires to utilize a part of the mononitrotoluene and dinitrotoluene products for purposes other than the preparation of TNT. But if it is desired to convert the toluene wholly into TNT and no regard is had to intermediate products, except in so far as these affect the quality and amount of the final product, method 3 seems to possess certain advantages. For the especial reason that method 3 eliminates the necessity of separation of the DNT mixture, the author selected it as most promising for

investigation and development in connection with the nitration of the water-gas toluene. Method 4 was tried only by way of comparison with the procedure finally determined on the basis of method 3.

CHARACTER OF TOLUENE USED IN EXPERIMENTS.

Results of Distillation.—A sample of the water-gas toluene (352.4 grams), dried over calcium chloride for two days, was distilled from a 700-c.c. flask provided with a Hempel still head 26.7 cm. in length. The results of distillation were as follows:

RESULTS OF DISTILLATION OF WATER-GAS TOLUENE.

Temperature interval, corrected, °C.	Weight of distillate, Grams.	Distillate, Per cent.
100 to 107.6.....	4.0	1.13
107.6 to 108.4.....	6.7	1.90
108.4 to 109.4.....	30.2	8.57
109.4 to 109.8.....	75.1	21.31
109.8 to 110.1.....	125.3	35.56
110.1.....	102.8	29.17
110.1.....	*8.2	*2.33
	352.3	99.97

*Remaining in still head.

The boiling point of pure toluene has been variously stated. Among the values given are the following: Landolt and Jahn,² 110° C.; Timmermans,³ 110.7° C. $\pm$ 1; Neubeck,⁴ 110.8° C.

A sample of the toluene as received, not dried, was distilled in a similar manner. The first 10 per cent of distillate (up to 108.4° C.) came over milky, indicating the presence of water.

Determination of Specific Gravity.—The specific gravity of the toluene was determined with a pycnometer. Duplicate determinations of the specific gravity of a sample of the toluene which had been dried over calcium chloride gave the values 0.8658 and 0.8660 at 20°/4° C.

The specific gravity at 20°/4° C. of the fraction of the toluene distilling at 110.1° C. (102.8-gram fraction mentioned under "Results of Distillation of Water-Gas Toluene," p. 13), determined in the same manner, was 0.8657.

According to Landolt and Jahn, the specific gravity of pure toluene at 20°/4° C. is 0.86542. Calculated from their formula:

$$d_{20}^{20} = \frac{t}{4} = 0.88418 - 0.00091961t$$

$$d_{20}^{20} = 0.8658.$$

Freezing Tests.—A sample of the toluene after standing over calcium chloride for one week was cooled in a test tube to -17° C. in an ice-salt cooling mixture. At this temperature there was a separation of a small quantity of white solid which when warmed again to -12° C. entirely disappeared. A

sample of the fraction distilling at a temperature of 108.4° to 109.4° C. (see "Results of Distillation of Water-Gas Toluene," p. 13), behaved in the same manner. From the 110.1° distillate no such separation of solid occurred at -17° C.

One drop of pure benzene was added to a part of the 110.1° distillate. At -15° C. there was a separation of solid which melted again at -7° C. A drop of water added instead of the benzene to a part of the same distillate caused a separation of solid at -15° C., which persisted up to +5° C.

A sample of the original toluene dried over calcium chloride was cooled in a test tube by means of a mixture of acetone and solid carbon dioxide. At -65° C. the total solid material separated was estimated as amounting to less than 1 per cent of the sample. This melted completely at about -12° C. There was no apparent increase of solid material separated at -77.5° C. At -79.5° C. less solid separated from the 110.1° fraction than from the dried toluene itself.

A sample of the dried toluene was cooled in a bath of gasolene cooled by means of liquid air. The whole solidified at -91° C. (uncorrected reading). It nearly all melted at -50° C. The freezing point of toluene as determined by Guttman⁵ is -92.4° C. No identification of the approximately 1 per cent solid separating as low as -79.5° C. was attempted.

Dimethylsulphate and Sulphonation Tests for Paraffins.—The well-known dimethylsulphate and sulphonation tests for paraffins both gave negative results, but those tests were scarcely to be relied on in this connection.

The distillation experiments, specific gravity determinations, freezing tests, and dimethylsulphate and sulphonation tests indicated a high degree of purity for the toluene. The presence of some water and probably also of benzene was indicated. Whether other impurities were present and, if so, their nature was not established. However, the tests showed that the total impurities did not exceed approximately 1 per cent, and that figure was borne out by nitration experiments later described.

PREPARATION OF MONONITROTOLUENE.

The first step in the nitration of toluene was performed in a simple apparatus consisting of an ordinary wide-mouth bottle, of approximately 1-liter capacity, provided with a glass stirrer propelled by a small motor, and placed within a larger glass vessel through which water of the required temperature was allowed to flow. Temperature readings were made by means of an ordinary thermometer. The nitrating acid was placed in the bottle and the toluene was introduced slowly, with constant stirring of the acid mixture, or the reverse procedure of adding the acid to the toluene was followed.

²Landolt, H., and Jahn, Hans, *Molekularfraktion*, etc.: Ztschr. phys. Chem., Bd. 10, 1892, p. 292.

³Timmermans, J., *Sur la purification et les constantes physiques de quelques liquides organiques*: Bull. Soc. chim. Belg., t. 24, 1910, p. 265.

⁴Neubeck, F., *Über Molekularvolumina aromatischer Verbindungen*: Ztschr. phys. Chem., Bd. 1, 1887, p. 656.

⁵Guttman, L. F., The determination of melting points at low temperatures: Jour. Chem. Soc., vol. 87, 1905, p. 1042.

The details of two experiments designated "Procedure A" and "Procedure B," are given below as illustrating the method and indicating the character and yield of the product:

Procedure A.—To 200 grams of toluene cooled to 9° C. by ice water in the cooling vessel a mixture of 587 grams of sulphuric acid of 1.84 specific gravity and 293.5 grams of nitric acid of 1.42 specific gravity (50 per cent in excess of theoretical nitric acid) was slowly added from a dropping funnel, with constant stirring of the contents of the bottle. The addition of the acid and the cooling of the reacting mixture were so regulated that a temperature of 20° to 30° C. was maintained during the greater part of the operation. Owing to loss of control the temperature was as high as 30° to 50° C. for a few minutes in the early part of the operation. The time consumed in completing the introduction of the acid was 1 hour and 20 minutes. Afterwards the water in the cooling vessel was run out and stirring continued one-half hour longer. After standing over night in a separatory funnel, the spent acid and the nitration product, a clear light-yellow liquid, were separated. The yield of crude MNT as thus separated was 320 grams.

Eighty grams of this crude product, corresponding to the yield from 50 grams of toluene, was carefully washed with water till free from acid, dried over calcium chloride for several days, filtered, and weighed. The acid washings were made slightly alkaline with sodium hydroxide, and were extracted with ether. The ether solution dried over calcium chloride was used for extracting the MNT adhering to the flask and in the chloride used in drying the other larger fraction of the product. The total weight of MNT thus obtained was 71.5 grams. This product had a specific gravity of 1.1818 at 22° C. and a nitrogen content of 10.58 per cent. Pure MNT contains 10.22 per cent nitrogen, and crude MNT, according to Escalas, has a specific gravity of approximately 1.165. Fifty grams of pure toluene yields theoretically 74.46 grams of MNT.

For further nitration the crude unwashed product was used, so that no losses due to purification had to be considered.

Procedure B.—In the second experiment the same weights of toluene and acids were used as in the first, but the toluene was added to the acids. Otherwise the procedure was the same. Little difficulty was experienced in maintaining a temperature of 13° to 30° C. during the operation of mixing, which lasted two hours. As before, the stirring was continued one-half hour after the mixing had been completed. The yield of crude product was 331.4 grams. Purified as above, 248.55 grams yielded 243.4 grams, having a specific gravity of 1.2450 and a nitrogen content of 12.14 per cent.

The high values for specific gravity and nitrogen were due to the formation of considerable dinitrotoluene, as the following data regarding the product show:

RESULTS OF DISTILLATION OF 111.8 GRAMS OF CRUDE MONONITROTOLUENE AT A PRESSURE OF 30 MM.

Fraction.	Temperature interval, ° C.	Weight of fraction.	
		Grams.	Per cent.
A	115 to 160	68.1	60.91
B	162 to 185	40.7	36.41
Residue		2.5	2.68
Loss		0.5	

Fraction A was a liquid having a specific gravity of 1.1750 and a nitrogen content of 10.34 per cent, or practically pure MNT, which contains 10.22 per cent nitrogen.

Fraction B was a white solid mass containing 15.13 per cent nitrogen, or nearly pure DNT, which contains 15.38 per cent nitrogen.

Calculated from the data of the nitrogen determination of the purified products before distillation, the values of 62.93 per cent and 37.07 per cent are obtained for the mononitrotoluene and dinitrotoluene contents, respectively, which are in close accord with the distillation values. These calculations are necessarily based on the assumption that only MNT and DNT were present.

A further simple calculation is as follows: One hundred grams of toluene yielded 162.26 grams of purified product, or 102.11 grams of MNT (62.93 per cent) and 60.15 grams of DNT (37.07 per cent). The latter quantity of DNT corresponds to 45.28 grams MNT. Hence the 100 grams of toluene yielded a total of 147.39 grams of MNT which in turn corresponds to 98.98 grams of toluene.

In view of the above results it is evident that Procedure B can not be followed if the nonformation of dinitrotoluene is desired. In that case, of the two procedures, Procedure A must be followed instead. Other experiments indicated, however, that Procedure B may be used with little formation of DNT, provided the excess of nitric acid over the theoretical amount required for the nitration is small. But under such conditions some of the toluene will escape nitration; the product obtained in one experiment in which an excess of 25 per cent nitric acid was employed had a strong odor of toluene. In the use of less than 40 to 50 per cent excess nitric acid in Procedure B, the further difficulty of maintaining the progress of the reaction and also of avoiding the formation of very dark reaction mixtures, often of dark sludge, resulting frequently in the impossibility of separating the product from the spent acid, is to be ascribed to the depletion of the nitric acid by the formation of DNT. With 50 per cent excess nitric acid, however, no such difficulty was experienced, and if the temperature of reaction was not allowed to exceed 50° C., the resultant product was a clear yellow liquid from which the spent acid was readily drawn. If, on the other hand, a greater excess of nitric acid than 50 per cent is employed for nitration, the proportion of DNT formed may be large enough to result in its separation from solution in the liquid MNT, with consequent difficulty in effecting a separation of the product from the spent

acid, and in the possible difficulties encountered when TNT is prepared from DNT. In one experiment 50 grams of toluene treated with an acid mixture containing 100 per cent excess nitric acid yielded 90 grams of a crude product which was almost entirely solid DNT.

Inasmuch as the resultant crude product designated as MNT is to be used for the preparation of TNT, the formation of DNT is of much less consequence than is the loss of toluene, and besides some 40 per cent of the 50 per cent excess nitric acid is used up in converting a part of the MNT into DNT. For these reasons and because the temperature of nitration was easier to control than in Procedure A, Procedure B was followed in the preparation of the MNT in most of the experiments. In general, effort was made to keep the temperature of reaction below 30° C., and no subsequent heating was required. But the experiments did not show that a temperature as high as 50° C. either decreased the yield or affected seriously the character of the product.

Table I following gives data regarding the experiments upon which the above conclusions are based:

PREPARATION OF TRINITROTOLUENE FROM
MONONITROTOLUENE.

The preparation of trinitrotoluene from the crude mononitrotoluene was accomplished in an apparatus similar to that used in the preparation of the MNT. The vessel in which the nitration was effected was a tall beaker without lip, which was 23 cm. high and

had a diameter of 8 cm. The beaker was placed on a sand bath, which could be heated with a gas burner as desired. To serve as a cover for the beaker a Florence flask from which the bottom had been removed, and to which a second neck about 1 cm. in diameter had been sealed at a distance of about 3 cm. from the original neck and parallel to it, was placed so as to fit closely on the flange of the beaker, the necks extending downward for about 6 cm. into the beaker. Through the smaller neck a thermometer was inserted; the larger neck equidistant from the sides of the beaker carried the glass stirrer and served as the opening through which the acids were dropped from a separatory funnel. The temperature of nitration was controlled by varying the rate at which the nitrating acid was added and by raising or lowering the flame.

At the completion of each operation the reaction products were allowed to cool to about 100° C., when they were transferred to a specially constructed separatory funnel by means of which a hot separation of the liquid nitration product was made; or, as was the general procedure, the contents of the funnel were allowed to stand about 18 hours, during which time the supernatant liquid TNT would solidify as a hard cake, and the dissolved TNT would crystallize out beneath. The spent acid was drained off from below. The solid cake of TNT from either procedure was crushed, combined with the remainder of the solid separated, and washed well with cold water. After-

TABLE I.—DATA REGARDING EXPERIMENTS COVERING PREPARATION OF MONONITROTOLUENE FROM TOLUENE.

Experiment No.	Weight of toluene. Grams.	Per cent of nitric acid in excess of theoretical.	Ratio of nitric acid to sulphuric acid.	Temperature of mix- ing. °C.	Time of mixing. Minutes.	Subsequent heating.	Yield of crude MNT. Grams.	Yield of acid-free and dry MNT. Grams.	Specific gravity of acid- free and dry MNT.	Per cent of nitrogen.	Remarks.
1..	50	10	1:3	20 to 30	30	1½ hours at 90° to 95° C.	72				Dark-green mix- ture; no separa- tion.
2..	50	10	1:3	25 to 35	35	1 hour up to 95° C.; 2 hours at 95° to 97° C.					
3..	50	25	1:3	20 to 30	25	None	74.0	67.3			Dark-red product; odor of toluene.
4..	50	25	1:3	25 to 55	20	2 hours up to 94° C. ^a					Black mixture; no separation.
5..	50	40	1:2	25 to 50	25	None	79.0	75.7	1.2194	11.37	
6..	50	50	1:1.5	20 to 30	25	1 hour up to 70°; 1 hour at 70° to 85° C.; 3 hours at 85° to 90° C.	81.0				
7..	50	50	1:1.5	20 to 30	40	A few minutes at 50° C.	81.0				
8..	50	50	1:2	25 to 30	40	2 hours up to 97° C.; 2 hours at 93° to 97° C.	82.0				
9..	50	50	1:2	25 to 30	25	None	82.0	78.0		11.36	
10..	50	50	1:2	25 to 55	25	None	81.0	78.2	1.2400		
11..	50	100	1:2	20 to 30	45	4½ hours at 90° to 95° C.	90.0				Product mainly solid dinitro- toluene.
12..	50	50	1:2	25 to 30	40	½ hour up to 95° C.; ½ hour at 95° to 97° C.	81.8				
13..	100	50	1:2	22 to 49	35	None	165.1				
14..	100	50	1:2	25 to 58	18	None	164.0				
15..	100	50	1:2	25 to 50	53	None	163.0				
16..	200	50	1:2	12 to 30	105	None	328.4				
17..	200	50	1:2	15 to 36	110	None	328.0	773.0			
18..	200	50	1:2	9 to 30	80	None	320.0	715.5	1.1818	10.58	Acid added to toluene.
19..	200	50	1:2	13 to 30	120	None	331.4	243.4	1.2450	12.14	

^a Excess HNO₃ increased to 50 per cent.

^b From 82 grams of crude product.

^c From 80 grams of crude product.

^d From 248.55 grams of crude product.

wards this was repeatedly washed in the molten condition with hot water until free from acid. When the spent acids were poured into approximately 5 to 10 volumes of ice water and ice a second lot of crude TNT was obtained and treated in the same way. The crude products were then dried either over sulphuric acid in a vacuum desiccator or in an electric oven at a temperature of 50° to 60° C.

If further purification of the crude TNT thus obtained was desired, this was accomplished by crystallization from a mixture of 9 parts of 95 per cent alcohol and 1 part of benzene, or by the simpler operation of shaking the finely powdered solid for a short time with a cold mixture of the composition mentioned.

FOUR SERIES OF EXPERIMENTS.

Four series of experiments covering the preparation of TNT from MNT were performed as outlined below.

Series 1.—In series 1 the mononitrotoluene was dissolved in 100 per cent sulphuric acid and nitrated with a mixture of equal parts by weight of nitric acid of specific gravity 1.5 and of 100 per cent sulphuric acid. The MNT used in each experiment was the total product obtained from the previous treatment of 50 grams of toluene. As 50 grams of pure toluene yields theoretically 74.46 grams of MNT, the latter figure was assumed to be the weight of the MNT in the crude product in calculating the amounts of nitric acid to be used in each experiment. To convert 74.46 grams of MNT into TNT requires theoretically 64.48 grams of anhydrous nitric acid or 72.78 grams of 94.09 per cent nitric acid having a specific gravity of 1.5.

Series 2.—In the experiments of series 2, with the exceptions noted in Table 2, following, the mononitrotoluene was dissolved in sulphuric acid having a specific gravity of 1.84, and was nitrated with a mixture of equal parts by weight of nitric acid having a specific gravity of 1.5 and of 100 per cent sulphuric acid.

Series 3.—In the experiments of series 3 the nitration of MNT may be considered as having been performed in two stages, but without a separation of the dinitrotoluene formed in the first stage of the nitration.

Except in one experiment, the MNT dissolved in sulphuric acid of specific gravity 1.84 was first treated with a mixture of equal parts by weight of nitric acid of specific gravity 1.5 and of sulphuric acid of specific gravity 1.84.

At the end of this stage in the nitration 15 per cent oleum was added to the reaction mixture to concentrate the acids, after which the nitration was completed with a mixture of equal parts by weight of nitric acid of specific gravity 1.5 and 15 per cent oleum.

Series 4.—In the experiments of series 4 trinitrotoluene was prepared from mononitrotoluene in two distinct steps involving the actual separation of the DNT formed in the first stage of nitration. The ex-

periments were made for the purpose of comparing the results with those of the experiments in series 3.

SUMMARY.

The results obtained in the experiments herein reported, especially those in experiments 4 and 5 of series 3, lead to the conclusion that the following procedure will give the best results in the preparation of trinitrotoluene:

OUTLINE OF MOST FAVORABLE METHOD OF PREPARING TRINITROTOLUENE.

The acid used in the first stage of the nitration of the toluene should be a mixture of two parts by weight of sulphuric acid of specific gravity 1.84 and one part of nitric acid of specific gravity 1.42, the weight of nitric acid taken being 50 per cent in excess of that required theoretically for the conversion of all the toluene into mononitrotoluene. For 50 grams of toluene 73.38 grams of nitric acid is used.

To the mixed acid contained in the nitrating vessel provided with apparatus for cooling and stirring, and cooled to 20° C. or lower, the toluene is added gradually, with constant stirring, the rate of introducing the toluene and the cooling of the reacting mixture being so regulated that the temperature does not exceed 30° C. When approximately 70 per cent of the toluene has been added, the nitration becomes much slower and little cooling of the mixture is required. When the total amount of the toluene has been introduced and the temperature ceases to rise, the cold water surrounding the nitrating vessel is allowed to run out while the operation is continued about one-half hour longer. After the contents of the nitrating vessel have stood for some time, preferably over night, the spent acids are removed by gravity from the supernatant crude mononitrotoluene, which consists of a mixture of mononitrotoluenes and dinitrotoluenes.

PREPARATION OF TRINITROTOLUENE FROM MONONITROTOLUENE.

First Stage.—The mixed acid used in the first step in the conversion of the crude mononitrotoluene into trinitrotoluene consists of equal weights of sulphuric acid of specific gravity 1.84 and of nitric acid of specific gravity 1.5, the nitric acid content being 50 per cent in excess of that required theoretically to convert the calculated yield of mononitrotoluene into dinitrotoluene. For the product derived from 50 grams of toluene, 54.58 grams of nitric acid is taken.

The crude mononitrotoluene is dissolved in sulphuric acid having a specific gravity of 1.84, the weight of the acid being equal to the weight of mixed acid, and is heated to 50° C. The mixed acid is added gradually, with constant stirring, over a period of at least one hour, during which time the temperature should not exceed 100° C. After all the acid has been introduced, the mixture is heated for two hours at a temperature of 90° to 100° C.

Second Stage.—At this point the acids in the nitrating vessel, cooled to about 90° C., are concentrated by the addition of 15 per cent oleum, equal in

weight to the weight of the mixed acid to be used in completing the nitration. If the oleum is added slowly, little rise in temperature occurs.

The mixed acid used consists of equal weights of nitric acid (specific gravity, 1.5) and 15 per cent oleum, the nitric acid taken being double that required theoretically to convert into trinitrotoluene the nitration products calculated as dinitrotoluene. On the basis of 50 grams of toluene, 72.78 grams of nitric acid is used.

The mixed acid is added gradually, with continued stirring, while the temperature is allowed to rise up to but not above 115° C. When approximately 75 per cent of the acid has been introduced, heating is required to maintain the temperature above 100° C. A minimum time of two hours should be allowed for the introduction of the acid. When the addition of acid has been completed, the heating is continued for two hours longer, a temperature of 90° to 117° C. being maintained, but the latter temperature should not be exceeded.

Upon the completion of the nitration the reaction mixture is allowed to cool in a vessel adapted to the subsequent removal of the spent acid. After standing at least 18 hours, the crude trinitrotoluene will have separated as a solid cake and suspended crystals. After the underlying spent acid has been drained off, the crude product is crushed, washed well with cold and hot water, dried, etc., as previously described. A higher degree of purity may be obtained by washing with the alcohol-benzene mixture.

The spent acid contains in solution additional trinitrotoluene as well as lower nitration products, which may be recovered by precipitation in water. In practice the spent acid is used over again after renewal by the addition of fresh acids.

The possibilities of utilizing the kaing grass of Burma for paper making have for some years past been investigated by persons interested, in consultation with paper manufacturers in this country, and it is now announced that the conversion of this grass into pulp and subsequently into paper can be accomplished in a simple and economical manner. It is expected that arrangements will soon be completed for the collection of the grass, its conversion into pulp, and its shipment in this form to paper makers in the United Kingdom.

Coal-gas plants in the United States in 1915 produced and sold 336,213 gal. benzol, drip oil, and holder oil, valued at \$28,281, an average value of 8.4 cents a gallon. Benzol products recovered in connection with the manufacture of by-product coke amounted to 16,600,857 gallons, valued at \$7,337,371, an average of 44.2 cents a gallon. It is thus seen that coal-gas plants are negligible as a source of supply of benzol products.

THE BRITTLINESS OF ANNEALED COPPER.*

By W. E. RUDER.

In the process of manufacture of commercial copper, it has been found advisable to leave a certain amount of oxygen in the copper in order that it may retain the very desirable properties of ductility and mechanical strength. The ease with which copper takes up oxygen during smelting makes it necessary that this oxide be removed by the process of "poling," during which the oxide is reduced by the gases given off by the green poles. This process is carried on until only the small amount of oxygen necessary to produce "tough pitch" copper remains. This oxygen exists in practically all commercial copper, not specially deoxidized, in the form of Cu_2O and forms a matrix of eutectic around the primary copper grains.

It is common practice in annealing copper to maintain a strictly neutral or slightly oxidizing atmosphere. In the practice of the process of calorizing (Trans. Am. Electrochem. Soc. 27, 253, 1915) it was found that copper articles became quite brittle even at temperatures as low as 500° C. In forging and working copper it is also necessary to have the atmosphere of the heating furnace pretty well regulated, or the whole lot will become unworkable.

Copper rail bonds made up of strands of commercial copper wire, heated in an oil muffle during the process of manufacture, frequently and irregularly showed brittleness as though burned, but there was no sign of oxidation. It was assumed that the harmful effect was due to reducing gases from the fire which sometimes come into direct contact with the copper. To demonstrate this, an experiment was tried as follows: Two quartz tubes were placed into a vertical electrically-heated furnace. One was closed and the other open at the lower end, while the upper ends of both tubes were open and extended outside the furnace. Commercial copper wires were placed in each of these tubes. Hydrogen gas was fed into the furnace and came into contact with the wires in the open tube, but not with the others. The result of heating to red heat for ten minutes in this case was the apparent rotting of the wire in the tube open at both ends but not in the tube closed to the hydrogen.

Further evidence that this brittleness is due to the action of the reducing gases upon the dissolved oxygen is had from the fact that copper to which boron carbide or some other deoxidizing agent has been added does not show this effect. It is the purpose of this paper to report the result of a few experiments made to determine the effect upon regular and deoxidized copper, at different temperatures, of a few of the more common gases met with in practice.

*Paper presented at the 29th general meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

Cuprous oxide may be reduced by hydrogen or carbon monoxide at temperatures as low as 200° C. Some effect must therefore be expected, even at temperatures below those usually employed in annealing.

In these experiments wires of plain 0.15 in. (3.8 mm.) and boronized 0.125 in. (3.2 mm.) copper were used. It was soon found that smaller wires were more sensitive to exposure for a short time at the lower ranges, and so a piece of 0.05 in. (1.3 mm.) wire of each kind was also used in each run. No accurate measurements of brittleness were made, as a simple bending test was sufficient for our purpose. If a wire would not stand bending to a right angle and back without cracking, it was termed brittle. Samples were run at 100° intervals from 400° C. to 1,000° C. and held for two hours.

EFFECT OF HYDROGEN.

Electrolytic hydrogen, purified by running over hot copper and thoroughly dried over P_2O_5 , was used.

Commercial Copper.—At 400° C. no brittleness could be detected after a two hours' anneal. After 31 hours' anneal, however, a decided weakening had occurred.

At 500° C. the smaller wires were quite brittle after two hours, and the large one cracked on the surface, showing that the action had started.

At 600° C. the brittleness had penetrated about 3/64 inch (1.2 mm.) on the large piece, and the small wire was extremely brittle.

At 800° C. the large wire became so brittle that it broke on bending through an angle of 10°.

At 1,000° C. the copper was still brittle, but showed a marked tendency toward recovery.

On remelting in hydrogen the copper was restored to its original ductility.

Deoxidized Copper.—Copper, which had been deoxidized by the addition of boron in the form of boron carbide, and run through the same treatment as the regular copper samples above, in no case exhibited the least trace of brittleness.

EFFECT OF WET HYDROGEN.

Hydrogen bubbled through water had the same effect as the purified hydrogen, except that the brittleness did not appear until a temperature of 600° C. was reached. Deoxidized copper was not affected at any temperature.

EFFECT OF CARBON MONOXIDE.

Brittleness was not observed in this treatment until a temperature of about 850 to 900° C. was attained. At 900° C. and 1,000° C., however, extreme brittleness was caused in two hours. As in previous cases, boronized copper was unaffected. The high temperature needed to produce brittleness in this case was probably due to the presence of considerable CO_2 mixed with the CO. The CO gas was made by passing a slow stream of air over incandescent charcoal. The samples were all somewhat oxidized on the surface.

EFFECT OF CARBON DIOXIDE.

Tank CO_2 dried over sulphuric acid was used in these experiments. The samples scaled quite severely at the higher temperatures, but no perceptible brittleness occurred in any of the samples except the boronized copper run at 900° C. and 1,000° C. This result was rather unexpected, and the reason why this deoxidized copper should be more brittle than the regular copper under these particular circumstances is not yet clear, as oxidation should have made each one brittle.

EFFECT OF STEAM.

A slight brittleness was observed in regular copper at 700° C. This increased with the temperature, but in no case was the material as brittle as that treated in hydrogen or CO gas. An explosion of the hydrogen gas occurred at the mouth of the furnace running at 1,000° C.

SUMMARY.

It has been shown that the brittleness of copper developed during heating in the process of manufacture and frequently ascribed to "burning," is in reality a deoxidation. With ordinary commercial copper, serious brittleness begins to appear at 400° C. in dry hydrogen, at 600° C. in wet hydrogen, at about 800 to 850° C. in CO, and at 700° C. in steam. Copper which had previously been deoxidized by the addition of boron remains unaffected at all temperatures in a reducing atmosphere. This brittleness is therefore due to the reduction of the cuprous oxide around the primary copper grains, leaving a spongy mass of little mechanical strength, and not to any direct action of the hydrogen upon the copper itself.

SALT PRODUCTION.

In the production of that indispensable condiment, salt, the United States is happily independent of all other countries. The 38,231,496 barrels of salt produced in 1915 by 14 states, Porto Rico, and Hawaii constituted 99 per cent of the salt consumed in the United States, and much more could easily have been supplied had the demand required it, according to the United States Geological Survey, Department of the Interior. Salt occurs naturally in two distinct ways—as rock salt, in beds or associated with bedded or sedimentary deposits, and in natural brines. The larger part of our salt is obtained by converting rock salt that lies deep below the earth's surface into artificial brines, which are pumped to the surface and there evaporated. Some idea of the quantity of salt evaporated from natural brines may be gained from statistics of the output of New York, Michigan and Kansas alone, three large salt-producing states, for the calendar year 1915. In Michigan, 6,708,261 barrels of evaporated salt, having a value of \$3,635,692, were produced; in New York, 3,443,464 barrels, valued at \$1,720,434; and in Kansas, 1,901,756 barrels, valued at \$696,060.

RESEARCH AND TESTING.*

By PRESTON S. MILLAR.†

In previous articles qualifications which make for the success of the young engineer have received attention. Such qualifications are in part natural and in part acquired. Furthermore, they are found in various degrees. All of them under favorable conditions and by determined effort may be developed from a lesser to a greater degree. The young engineer confronting a choice of occupation does well to consider not alone prospects for early professional or financial advancement. His choice should be influenced also by opportunity to acquire or to develop qualifications for ultimate success.

It is this consideration which brings into relief research and testing as an occupation to be considered by the young electrical engineer. This field offers exceptional opportunities for acquiring important qualifications for success. Prominent among these is the "scientific state of mind" or the "scientific viewpoint" which the writer wishes to add to those indicated in this series.

THE SCIENTIFIC VIEWPOINT.

The scientific viewpoint is of well-nigh universal applicability. Essential in research, indispensable in engineering, its value in the industrial or commercial world is fast gaining recognition. It underlies scientific management or efficiency engineering, which in one form or another is manifesting itself in all human activity.

This viewpoint once acquired is brought to bear upon all tasks and problems through a series of processes which roughly are as follows:

1. Definition of purpose.
2. Analysis of problem and listing of all variables.
3. Study of related literature and experience.
4. Adoption of approved methods.
5. Proving of method and appliances.
6. Proper conduct of research (or test or other enterprise).
7. Discussion of results.
8. Limitations of conclusions.

To apply this or a similar procedure completely or in part to all phases of industry; to investigate each subject along these lines with as much care and diligence as its importance may warrant; to ascertain the facts which it is important to know; to act logically in the light of such facts—this follows upon the adoption of the scientific point of view.

The man who can discern an opportunity or a need, who, within the limits of his knowledge and experience, is able to decide what action should be taken in the circumstances and who acts accordingly, possesses more than mere executive ability. Such a man will go far, especially if he displays the other sterling

qualities which have been emphasized in this series. This combination of perspicacity, decision and action is a trait which may be developed to some extent. And an important aid to its development is the acquisition of the scientific viewpoint.

The writer of the introductory article of this series distinguished between the "business" and "laboratory" type of man, intimating that in the future these two types are likely to merge successfully. This may be considered in connection with the unrelated facts of vocational fortuity and increasing specialization. If our industry suffers from misfits and if training tends toward narrow specialization, it is important to inculcate the fundamental principles which are the prerequisites of success. Application of such principles tends to reduce in extent the misfitting and to mitigate the evils of excessive specialization. It likewise promotes the merging of the "laboratory" and "business" type. Among these principles the scientific method must be conceded an important place.

But the scientific viewpoint contributes not alone to material success. We find things uninteresting only when we know too little about them to appreciate their potential interest. When viewed in the scientific spirit, everything becomes interesting. The scientific viewpoint develops interest, promotes investigation and inspires to further achievement.

THE ADVANTAGES OF LABORATORY WORK.

The engineering course affords the undergraduate opportunity to acquire the scientific state of mind, as does also engineering practice. But work in a research or testing laboratory is especially favorable to its acquisition. Knowledge gleaned from personal experience is more useful and significant than that acquired from others. Scientific methods become habitual only through practice. A laboratory is a fact factory. To seek facts, either with or without reference to their application, is to foster the scientific spirit, which through practice becomes thoroughly ingrained and constitutes an important qualification for success.

Work in a laboratory develops manual dexterity, trains observation, teaches necessity for predicating conclusions upon facts only.

Research and testing often afford an opportunity to gain a diversified knowledge of materials and apparatus. This knowledge, if limited to laboratory performance, may be inadequate in that the practical service experience is lacking. On the other hand, so far as it goes, it is soundly based upon facts. It is the best possible foundation upon which to erect an operating experience. Also it is an excellent safeguard against the temptation which so often assails practical engineers to draw conclusions from impressions founded upon inadequate data compounded of effects of variables which have not been segregated.

Laboratory work may bring the young engineer into contact with several phases of the industry, in-

*From The Electrical World.

†General Manager Electrical Testing Laboratories, New York City.

cluding manufacturing, selling and both the engineering and commercial branches of electrical operation in the several fields. While such contact usually is casual, yet it frequently takes place in those phases of the work which offer the most interesting engineering opportunities. Work of this kind occasionally affords the young engineer means of becoming known favorably in one or more branches of the industry. The experience gained should be developmental, widening the outlook.

If the laboratory is engaged in industrial research or in commercial testing, the work may afford the young engineer an opportunity to acquire knowledge of the viewpoints and methods of both manufacturer and consumer, seller and buyer. This lends business perspective.

CONDITIONS IN THE LABORATORY FIELD.

The opportunities for employment in electrical research and testing are relatively few. The government laboratories, notably the Bureau of Standards, are one class of employers in this field. There are a few small private laboratories. Large manufacturing corporations in increasing numbers are maintaining research laboratories. Large operating corporations in increasing numbers are maintaining testing laboratories. While this field is being extended and expanded, yet it can offer employment yearly to only a very limited number of young men. The largest electrical manufacturers yearly employ considerable numbers of graduates in an apprentice course. The scope of their engineering departments comprehends a certain amount of investigation work. Both offer excellent opportunity for acquiring useful experience and some opportunity for acquiring the scientific viewpoint.

The successful research man must possess somewhat unusual qualities with which few are endowed. But a small proportion of engineering graduates will look forward to making research or testing a life work. For these few, employment in a laboratory is of course immediately desirable. The great majority, by force of circumstances, inclination or training, will be directed into other branches of the industry. Many ultimately will find their way into designing, manufacturing, operating, commercial or consulting work.

Remuneration in research and testing for the young engineer probably averages about as in the manufacturing and operating branches of the industry. Later compensation, of course, depends upon merit and opportunity as in other forms of business. A small branch of the electrical industry, testing, offers fewer important and highly remunerative positions. On the other hand, there are few men eligible for such positions. Upon the whole there is probably little ground to select or to avoid research and testing for reasons of compensation only.

TUNGSTEN PRODUCTION DURING FIRST SIX MONTHS OF 1916.

The tungsten production of the United States during the first six months of 1916 exceeded the production of this or any other country in any previous twelve months. Prices were even more phenomenal than production and reached more than ten times their ordinary level. The output was equivalent to about 3,290 short tons of concentrates carrying 60 per cent WO_3 , valued at \$9,113,000, according to an estimate made by Frank L. Hess, of the United States Geological Survey, Department of the Interior. Statistics are valuable only so far as their accuracy is known, and this estimate is believed to be correct within 10 per cent and to be under rather than over the true figures.

These figures are no less noteworthy when it is known that in 1915 much the larger part of the production was in the second half of the year, so that the total domestic output for the twelve months ending June 30, 1916, probably amounted to about 5,000 tons.

Not only were the output and prices unique, but the ratio of the several tungsten minerals produced was different from that of other countries of large production. The quantities and values were approximately as follows: Ferberite, 1,495 tons, \$3,590,000; scheelite, 1,404 tons, \$4,322,000; wolframite, 201 tons, \$613,000; and hubnerite, 185 tons, \$587,000.

Prices at the beginning of the year were irregular and depended on the buyer's need of the ore and probably on his fear of the possibility of not being able to get it when he might need it even more. Ores carrying 60 per cent tungsten trioxide brought at that time as much as \$66 a unit, but by the last of March some ferberite sold for \$93.50 a unit at the mills, and even higher prices were quoted in the newspapers, though they could not be confirmed. The prices of the same ore in the New York market would naturally be somewhat higher. Under the stimulus of these high prices production, not only in this country but in the world at large, has been at the highest point ever known. At first the sudden demand created by the orders for war steel were far ahead of the instant productive power of the country. The rapid increase in prices, starting last fall at a time when tungsten mining was at a low ebb and culminating in the undreamed maximum mentioned, caused prospecting and consequent discoveries of new deposits, increase of development of known deposits, the operating at high tension of old mills, and the hasty building of new mills. As a result, the production increased faster than the consumption and soon overran the demand that would absorb the output at the extremely high prices prevailing, so that a drop in prices was inevitable. June closed with the price around \$25 a unit, which was still much higher than any price known before this year. The highest price previously reported to the Geological Survey was

\$15 a unit, paid in 1907. The normal price has been \$6 to \$7.

One of the most interesting developments of the year was the beginning of production of scheelite from contact-metamorphic deposits. Two deposits of this sort near Toy (Browns), Nev., were exploited, and near Bishop, Cal., mills of 30 and 100 tons were erected on similar deposits. Other contact deposits were located a few miles south of Bishop. It is thought by the Bishop mill owners that their claims can be worked profitably under such prices as were paid before the war. Tungsten minerals added largely to the receipts of gold mines at Lead, S. Dak., and White Oaks, N. Mex.

The consumption of tungsten in the United States was even greater than was indicated by the ores produced, for all parts of the world free from the control of the warring European nations were drawn on for supplies, and during the first five months of the year 1,520 tons of tungsten ore, valued at \$3,449,311, were imported. The June imports were probably equal to the average of the five preceding months, making the total for the half year 1,824 tons, valued at \$4,139,000. Some of the ore imported is known to have been of low grade, but a considerable quantity carried more than 60 per cent tungsten trioxide, and probably the average was not far from 60 per cent WO_3 . Most of the ore came from South America—Peru, Bolivia, Argentina, and a little from Brazil—but some ore came from Japan and Mexico. Some of that imported, like a little of the American ore, contained phosphorus, arsenic, copper, and other harmful impurities, but during the height of the demand even this ore was readily bought. By June buyers became more careful and it was not so easy to sell bad ore.

Ten tons of tungsten metal and ferrotungsten, valued at \$36,885, were recorded as imported. The exports for the first five months of the year amounted to 4,006 pounds, valued at \$10,571.

If the American production and imports are added the consumption seems to have amounted, roughly to 5,100 tons of 60 per cent concentrates, valued at \$13,278,000. On the supposition that 20 per cent of the metal was lost in various operations, it seems probable that between 11,000 and 12,000 tons of new high-speed steels were made during the period, in addition to the steel made from tungsten saved from scrap and scale.

New Rates of Lyons' Silk Conditioning House.

The silk-conditioning house of Lyons, France, one of the largest and most important of its kind in the world, has modified its tariff on account of the increased cost of raw products, and especially of combustibles. The new schedule went into effect on October 1, 1916.

The operation of analyzing silk includes a qualitative and a quantitative chemical analysis. The tariff for

the former has not been changed and remains at 10 francs (\$1.93), whereas the latter has been increased from 4 francs (\$0.77) to 6 francs (\$1.16). The increase was due largely to the great scarcity and, when procured, to the high price of certain chemicals necessary to test and analyze various qualities of silk.

The tariff for weighing bales or boxes upon arrival at the conditioning house remains unchanged and is regulated as follows: Up to 220 pounds gross weight, \$0.04; above 220 pounds, per 50 pounds or fractions thereof, \$0.01.

DYE PRODUCTION IN THE UNITED STATES.

The public has received a good deal of mis-information, especially through certain articles in the public press, regarding the situation in the United States as to the production of colors or dyes. It is not generally known that the production of benzol, and similar products from which dyes are made, have been for years more than sufficient to produce all of the colors and dyes used in the United States, if the amount produced had been applied to these purposes. For years millions of gallons of benzol were employed in enriching illuminating gas, for lack of a better market, when the enrichment could have been easily obtained from other sources, and the benzol set free for color making. Our tar distillers have stood ready to furnish all the naphthalene, anthracene, and other materials beside benzol that are employed in making colors, and the ruling prices were well within the color makers' reach. The real difficulty has been the same that will confront us after the war, if our government does not take the necessary preventative measures. In the dye-making countries of Europe it is recognized that combination is the life of trade, not competition, and while American manufacturers who combine their brains and efforts to carry out the development of a great industry are regarded as criminals under the law, in European countries they are encouraged, and in fact are almost compelled to combine for the best good of the industry and the nation. The dye industry needs not more raw material, but intelligent protection against destructive competition, and encouragement and safety for the large investments necessary to develop the complicated and highly technical manufacturers. American manufacturers have the money and the will, and American chemists the brains and the knowledge, and while the great color industry cannot be developed in America over night, we have all the factors here that are required for success, if properly combined and fostered. *Dr. W. H. Blauvelt, Consulting Engineer, Semet-Solvay Co., Syracuse, N. Y., in the Proceedings, Engineers' Society of Western Pennsylvania.*

BY-PRODUCTS FROM COKE-OVEN OPERATIONS.

The value of by-products recovered from American coke manufacture in 1915 was nearly \$30,000,000, a large increase over the previous high-water mark of \$17,500,000 in 1914. Although there were material increases in the output and value of gas, tar and ammonia, which was to be expected with a greater output of by-product coke, the increase in benzol products presented the most interesting feature of the year in the coke industry. The value of these products rose from less than \$1,000,000 in 1914 to more than \$7,760,000 in 1915, according to the United States Geological Survey. Benzol has been recovered in this country from coke-oven gas for a number of years, but prior to 1915 the market was small and prices were low.

In 1914 there were 14 benzol plants in the United States, but they were all controlled by one company, and therefore it is not feasible to publish the statistics of their production for that or previous years. Last year 16 additional coke plants were equipped with benzol apparatus, and the output was very greatly increased.

The benzol products obtained in 1915 amounted to 16,600,657 gallons. More than 13,000,000 gallons of the total output was reported as crude light oil and had an average value of 33 cents. Some of the plants have their own stills and refineries, and the pure benzol reported from those sources amounted to 2,516,483 gallons, with an average value of nearly 57 cents, at least three times the value of crude benzol before the war, and 623,506 gallons of toluol, with an average value of \$2.45 a gallon. Crude benzol, which in 1914 was used to some extent for motor fuel, contained the toluol, which is now separated out and sold at fancy prices.

Quantities and values of by-products from coke-oven operations in 1915 were:

Product.	Quantity.	Value.
Tar obtained and sold, gallons.....	138,414,601	\$3,568,384
Ammonia obtained and sold:		
Sulphate, pounds	199,900,487	5,648,958
Liquor, gallons	10,626,612	1,240,473
Anhydrous, pounds	30,002,196	2,978,044
Gas produced, M cubic feet	213,667,614	
Surplus gas sold or used:		
Illuminating, M cubic feet	17,196,426	3,083,311
Domestic fuel, M cubic feet	27,590,624	3,158,129
Industrial fuel, M cubic feet	39,568,864	2,383,459
Benzol products:		
Crude light oils, gallons	13,082,678	4,301,281
Secondary light oils, gallons	182,039	28,739
Benzol, gallons	2,516,483	1,428,323
Toluol, gallons	623,506	1,529,803
Solvent naphtha, gallons	196,151	46,233
Naphthalene, pounds	465,865	46,959
Other products*		379,491
Total by-products		\$29,824,579
Coke, short tons	14,072,895	48,558,325
		\$78,382,904

*Includes breeze, retort carbon, domestic coke and coke dust, and aniline oil.

A METHOD FOR DETERMINING THE STRENGTH OF PAPER WHEN WET.*

By E. O. REED.

Ordinarily the strength of wet paper is not a matter of importance. Most kinds of paper when wet are very weak and break or tear with the greatest ease. Certain kinds of paper, however, must be handled while wet, and it is essential, therefore, that they have a sufficient wet strength to withstand this service. This is true of photographic paper, especially of blue and brown print paper, of bag and wrapping, of paper textiles and to a less extent of filter paper, and paper which is to be printed while wet. While papers may comply with the specified physical requirements under the usual conditions of temperature and humidity, they may prove entirely unsatisfactory for handling when wet.

It is a well-established fact that the moisture content of the paper has a great effect on paper making and testing, and considerable work has been done to determine the properties of paper under different temperatures and atmospheric moisture conditions. The strength of paper when wet, however, has received little attention. Beadle and Stevens¹ present an article on "The Dry and Wet Strengths of Paper." The exact method of carrying out the wet-strength test is not clearly stated and only the wet strength of papers used in the manufacture of paper yarns is dealt with.

Perhaps one of the most severe conditions to which paper is subjected when wet is in commercial blue and brown print developing. In this work sometimes paper 42 in. wide and 10 or 12 ft. long is handled while thoroughly wet. Much of the so-called blue-print paper will not withstand the necessary wetting without injury even though its other physical qualities may be entirely satisfactory.

The determination of the tensile strength of the wet paper has proved to be the most satisfactory test for indicating the strength required to withstand the washing necessary to insure permanent prints. The wet strength is determined by breaking a strip of paper of a definite width, after it has been immersed in water at a constant temperature for a definite period of time. A Schopper tensile strength machine, calibrated to read from 1 to 1,000 g., is used. The jaws of the clamps should open in front, so the ends of the wet strips may be inserted without injury, and are set 10 cm. apart, as a short strip of wet paper can be handled more easily. The test strips are cut 15 mm. wide and sufficiently long to allow for clamping in the machine. Tests are made in both the longitudinal and transverse directions. The strips are placed separately in a water bath at 70° F. for 20 min. After the specified time they are removed one at a time and

*From The Journal of Industrial and Engineering Chemistry.

¹Chem. News, 109 (1914), No. 2843, 242.

tested immediately. To obtain accurate results extreme care must be exercised in handling and clamping the wet strips to prevent injury to them.

The wet strength in the transverse direction of blue and brown print papers upon which most of this work has been done and also of Kraft and rope wrapping is less than 700 g. In the longitudinal direction 1,000 g. is an exceptionally high wet strength.

TABLE I—EFFECT OF TEMPERATURE OF WATER ON THE WET STRENGTH (GRAMS) OF PAPER, PAPERS WET FOR 20 MINUTES.

L & P No.	Kind of Paper.	Direction of Strip.	Temperature of Water Bath—°F.				
			50 G.	65 G.	70 G.	75 G.	100 G.
31470	Blue-print paper.....	Long.	679	610	563	536	346
		Trans.	346	285	282	288	219
31642	Blue-print paper.....	Long.	1000+	997+	988+	943	731
		Trans.	744	632	634	564	414
28517	Blue-print paper.....	Long.	1000+	1000+	1000+	1000+	1000+
	Bond.	Trans.	776	776	738	695	598
12956	Before sizing.....	Long.	631	621	604	585	492
		Trans.	300	271	258	258	222
12957	After animal sizing.....	Long.	918	824	754	754	578
	Parchment Bond.	Trans.	484	412	364	370	293
12914	Before sizing.....	Long.	600	536	464	474	398
		Trans.	270	251	224	228	187
12915	After animal sizing.....	Long.	850	773	704	674	495
		Trans.	406	329	309	309	240

Table I shows the effect of the temperature of the water on the strength. The length of time of wetting was 20 min. in all cases. From these results it is evident that in order to obtain concordant values the water in which the strips are wet must be maintained at a constant temperature. It will be noted that wide differences exist between results obtained on a paper wet at 50° F. and at 100° F. There is a progressive decrease in strength with rise of temperature of the water in which the papers are wet, and a difference of 5° F. in the temperature of the water makes a significant difference in the wet strength in the longitudinal direction, though the differences in the transverse direction are usually small: 70° F. has been adopted as the most suitable temperature at which to maintain the water bath.

Table II shows the effect of the length of time of wetting on the wet strength.

TABLE II—EFFECT OF IMMERSION IN WATER ON THE WET STRENGTH (GRAMS) OF PAPER. TEMPERATURE OF WATER BATH 70° F.

L & P No.	Kind of Paper.	Direction of Strip.	Time of Wetting—Minutes.				
			10 G.	20 G.	30 G.	45 G.	60 G.
31470	Blue-print paper	Long.	662	591	557	534	495
		Trans.	312	277	277	274	262
31471	Blue-print paper	Long.	487	446	434	438	420
		Trans.	257	236	226	222	222
30857	Bond paper	Long.	539	498	456	456	453
		Trans.	270	258	238	222	213
31632	Blue-print paper	Long.	1000+	908	850	813	793
		Trans.	562	489	464	409	414
28542	Blue-print paper	Long.	935	842	847	812	800
		Trans.	649	592	564	549	537

The figures show that it is necessary to immerse the paper for a definite time to obtain valuable and uniform results. The results obtained on paper immersed only 10 min. indicate, in most cases, that the water has not penetrated uniformly and the individual results are much more erratic than when the paper is

immersed for longer periods. After 20 min. immersion, which has been adopted as a suitable period for wetting, the individual results are more concordant though minimum results are not obtained in that time. The transverse strength is but little affected by even longer periods of immersion. In commercial practice blue and brown print papers are seldom in the water bath more than 20 min.

Table III shows the concordance of averages of 5 tests in each direction on the same paper made on different days under the adopted constant conditions of wetting for 20 min. at 70° F. Since the wet-strength tests are registered in grams and difficulty is experienced in handling and clamping the strips

TABLE III—DUPLICATE AVERAGES OF WET STRENGTH MADE UNDER THE SAME CONDITIONS.

Papers wet at 70° F. for 20 min.

L & P No.	First Average of Five.		Second Average of Five.	
	Long. G.	Trans. G.	Long. G.	Trans. G.
38541	812	521	829	531
31632	810	408	800	433
28540	690	376	690	385
31470	563	282	591	277
31471	416	224	426	221

of wet paper in the tester, these averages are considered very close. It is necessary to discard results on strips which have not been properly clamped. Care must also be taken not to put a strain on the strip while clamping.

Wet strength is apparently controlled by the kind of stock, length of fiber, character of beating, kind and quality of sizing and by the formation of the sheet.

Table IV shows that in every case the wet strength was considerably increased by animal sizing.

Owing to the impracticability of obtaining samples of paper made from the same stock by different methods of beating or beaten for different lengths of time or sized with different amounts of rosin or glue or both, it is not possible to show here in figures the effect of each of these factors nor to state exactly the factors and procedures which may produce a satisfactory wet strength.

In Table V are given complete results, including wet strength, on samples representative of various kinds of stock papers.

TABLE IV—EFFECT OF ANIMAL SIZING ON THE WET STRENGTH OF PAPER.

Papers wet at 70° F. for 20 min.			Wet strength, Pct. increase		
L & P No.	Kind of Paper.	Finish.	Long. Trans. due to sizing.		
			G.	G.	Long. Trans.
12956	Bond	Unsize	604	258	
12957		Animal sized	757	364	25.3 41.1
12963	Bond	Unsize	826	432	
12964		Animal sized	981	575	18.8 33.1
12914	Parchment Bond	Unsize	464	224	
12915		Animal sized	704	309	51.7 37.9
12916	Parchment Bond	Unsize	668	323	
12917		Animal sized	873	463	30.7 43.3
12918	Parchment Bond	Unsize	749	370	
12919		Animal sized	983+	483	31.2 30.5
12990	Bond	Uncalendered			
		unsize	270	162	
12989		Unsize	293	158	
12991		Animal sized	649	382	121.5 141.8
12993	Bond	Unsize	295	194	
12988		Animal sized	730	415	147.5 113.9

Examination of these results does not show a definite relationship between wet strength and any of the other characteristics of paper. A paper with a high wet strength will not necessarily exhibit satisfactory physical qualities under ordinary testing conditions or *vice versa*. While this is true, study of the subject has led to the opinion, however, that wet strength is controlled chiefly by beating, sizing and formation. High wet strength may be obtained with long stock beaten "wet," well matted and so sized as to render the fibers water-resistant.

A detailed study will be made of the effect of different papermaking procedures on wet strength, in order to reach more definite conclusions as to the factors affecting this characteristic of paper. Experience has demonstrated that by means of this test it can be determined whether a blue or brown print paper will withstand the customary washing without tearing.

The method promises to be of even greater utility in predetermining the behavior of bag and wrapping paper when wet, especially of cement and lime bags. Quantities of these materials are being shipped in paper bags, many of which tear readily when damp and offer no protection to their contents against moisture. The method will enable users of such bags

to determine whether they will prove satisfactory in service.

SUMMARY.

Wet strength is an essential property of paper for certain special uses. It is indicated by determining the tensile strength of wet strips, cut longitudinally and also transversely of the sheet. Strips 15 mm. in width and of sufficient length to allow a breaking length of 100 mm. are immersed in water at 70° F. for 20 min. and then tested in a machine calibrated to read in grams. It is important that the paper be immersed for a definite period of time and in water of a uniform temperature, as these factors greatly influence the test. Care must be exercised in making tests as paper is so easily injured when wet.

Wet strength is controlled by the combination of factors which influence other physical properties of paper such as length of fiber, beating, kind and quality of sizing and formation of the sheet, yet there is no direct relationship between the wet and dry strengths of paper. This test promises to be of value in predetermining the serviceability of paper used for bags, especially for cement and lime, wrapping, photographic, paper textiles and even paper which is to be printed while wet.

Dedication of the Ceramic Engineering Building of the University of Illinois.

The new Ceramic Engineering Building of the University of Illinois is to be formally dedicated on Nov. 20 and 21. The occasion will be made one of great interest to the clay workers of the country. It is expected that the exercises will be attended by many representatives of the architectural, structural, mining, geological, chemical, and manufacturing interests. In connection with the dedication exercises an industrial conference will be held, in which a number of topics of current interest to the ceramic engineer, the clay worker and the manufacturer will be discussed by well-known experts.

TABLE V—RESULTS OF EXAMINATION OF VARIOUS KINDS OF PAPER—ALL PHYSICAL TESTS MADE AT 70° F. AND 65 PER CENT RELATIVE HUMIDITY.

L & P No.	Paper	Stock (per cent).		Chem. wood.	Weight, 21x36 (600), lb.	Thickness, 1/1000 in.	Ash, per cent.	Sizing (per cent).		Starch.	Strength.	Tensile strength, Break Kg. Trans.	Folding endurance, Long. double.	Wet strength, 70° F., 20 min.						
		Tag.	Stuffed.					Animal	Rosin.						Trans.					
31899	Filter	100	...	...	43.5	73	0.2	0.0	0.0	Trace	12.0	0.22	2.6	2.1	0.8	1.3	6	5	100	66
31909	Printing	21	29	50	45.5	50	1.0	0.9	0.0	None	10.0	0.22	2.8	1.9	0.3	1.2	4	2	429	378
31910	Writing	52	48	...	52.5	39	1.2	1.1	0.6	Present	35.5	0.68	8.4	4.1	2.5	4.2	197	93	476	273
30857	Bond	100	...	...	40.0	30	0.8	1.8	4.2	Present	39.5	0.99	8.0	4.4	4.0	6.8	2686	877	527	249
30730	Bond	100	...	...	47.0	36	0.6	1.0	3.6	Present	47.5	1.01	9.0	4.6	3.7	6.3	1798	722	1000+	613
30856	Bond	53	47	...	46.5	33	0.6	1.6	1.5	Present	33.0	0.71	6.5	3.8	2.9	4.6	400	131	738	456
30858	Bond	...	100	...	48.0	38	2.3	1.2	0.0	None	26.0	0.51	7.6	3.7	1.7	4.0	164	98	673	290
28542	Blue-print	100	...	...	54.0	35	0.5	3.7	1.7	Present	42.0	0.78	6.5	5.4	3.5	7.0	1439	1308	808	629
28517	Blue-print	100	...	...	61.5	43	0.6	3.8	2.3	Present	42.5	0.69	9.2	5.3	2.5	4.9	265	135	1000+	661
31803	Blue-print	100	...	...	62.0	40	0.5	1.8	4.8	Present	76.0	1.23	13.8	7.6	3.9	6.6	3476	2666	947	528
31249	Ledger	100	...	...	51.0	36	1.0	1.0	3.5	Present	62.0	1.21	10.7	5.8	4.6	6.6	3489	1626	1000+	593
30855	Ledger	100	...	...	55.0	40	1.2	2.6	4.4	Present	59.5	1.08	10.8	5.9	5.3	7.7	2729	1266	926	512
31250	Ledger	...	100	...	47.5	36	3.6	1.5	0.0	Present	28.5	0.60	7.2	3.8	1.3	4.6	270	58	749	406
41922	Kraft	...	100 (sulphate)	...	57.0	50	0.9	0.7	0.0	None	43.0	0.75	9.4	4.2	1.7	3.7	1312	540	1000+	639
31921	Rope	...	91 (Jute)	...	87.0	90	2.8	2.0	0.0	None	111.0	1.30	14.6	5.8	3.0	6.1	2000+	3061	1000+	459

PRICES OF CHEMICALS, OILS, ETC., NOVEMBER, 1916

WHOLESALE PRICES PREVAILING IN NEW YORK MARKET ON NOVEMBER 17

CHEMICALS, INORGANIC.

Acetate of lime, 100 lbs.	\$ 3.50	@	3.65
Alum, ammonia, crystals, lb.	.04 ¹ / ₂	@	.04 ¹ / ₂
Aluminum sulphate, 100 lbs.	.04	@	.05
Arsenic, white, lb.	.06	@	.06 ³ / ₄
Barium chloride, ton	110.00	@	115.00
Barium nitrate, kegs, lb.	.14	@	.15
Bleaching powder, drums, 100 lbs.	4.75	@	5.00
Blue vitriol, car lots, 100 lbs.	13.00	@	
Blue vitriol, powdered, 100 lbs.	14.58	@	15.00
Borax, car lots, f. o. b. N. Y., 100 lbs.	7.50	@	8.00
Bristonite, crude, ton	35.00	@	
Caustic soda, 74 to 76%, lb.	.04	@	
Chalk, precipitated, cases, lb.	.06	@	.06 ¹ / ₂
Glanber's salt, bags, 100 lbs.	.60	@	.65
Nitric acid, 36 to 42°, 100 lbs.	7.50	@	8.00
Phosphoric acid, 1.750, lb.	.30	@	.34 ¹ / ₂
Potassium bichromate, lb.	.40	@	.42
Potassium carbonate, calcined, 90 to 96%, lb.	.80	@	.90
Potassium chlorate, crystals, lb.	.64	@	.67
Potassium cyanide, 94 to 96%, 100 lbs.	1.00	@	1.20
Quicksilver, flasks	80.00	@	82.00
Silver nitrate, ounce	.44 ¹ / ₂	@	.46 ¹ / ₂
Soda ash, 48%, 100 lbs.	2.50	@	2.55
Sodium acetate, lb.	.11	@	.12
Sodium bicarbonate, American, 100 lbs.	1.65	@	2.00
Sodium bichromate, lb.	.23	@	.24
Sodium chlorate, 100 lbs.	.30	@	.35
Sodium hyposulphite, in bbls., 100 lbs.	1.75	@	2.00
Sodium nitrite, lb.	.14 ¹ / ₂	@	.15
Sodium sulphide, crystals, 100 lbs.	2.50	@	3.00
Sulphuric acid, 60° and up, cwt.	1.50	@	2.00
Sulphuric acid, 66°, ton	33.00	@	35.00
Talc, domestic, spot, ton	15.49	@	
Tin, bichloride, 50°, 100 lbs.	14.25	@	
Tin, oxide, lb.	.48	@	.50

CHEMICALS, ORGANIC.

Acetanilid, lb.	\$.52	@	.55
Acetic acid, 28%, 100 lbs.	3.50	@	3.65
Acetic acid, glacial, 99 ¹ / ₂ %, carboys, lb.	.25	@	.30
Acetone, drums, lb.	.22 ¹ / ₂	@	.23
Alcohol, denatured, 188 proof, gal.	.62	@	
Alcohol, grain, 188 proof, gal.	2.72	@	2.74
Alcohol, wood, 95%, gal.	.85	@	.90
Amyl acetate, gal.	4.50	@	5.00
Benzoic acid, from toluol, cwt.	9.75	@	10.00
Carbolic acid, drums, crystals, lb.	.55	@	.58
Carbon, tetrachloride, lb.	.16 ¹ / ₂	@	.17
Chloroform, lb.	.50	@	.55
Citric acid, domestic, crystals, lb.	.67	@	.67 ¹ / ₂
Cresol, U. S. P., gal.	.75	@	.80
Ether, U. S. P., 1900, lb.	.15	@	.20
Formaldehyde, 40%, carboys, lb.	.11 ¹ / ₂	@	.12
Glycerine, dynamite, lb.	.50	@	
Pyrogalllic acid, crystal, lb.	3.15	@	3.50
Salicylic acid, lbs.	1.20	@	1.25
Tannic acid, technical, lb.	.90	@	1.00
Tartaric acid, crystals, U. S. P., lb.	.66	@	.66 ¹ / ₂

DYE MATERIALS.

Acid, orange, lb.	\$ 1.75	@	4.00
Aniline oil, drums, imported, lb.		@	
Aniline, domestic, lb.	.23	@	.25
Benzol (white), gal.	.57	@	.70
Bismarck brown, lb.	2.25	@	2.85

Carmine, lb.	4.50	@	4.60
Cochineal, silver, lb.	.65	@	.70
Cochineal, black, lb.	.70	@	.75
Gambier, lb.	.10 ¹ / ₂	@	.11
Indigo, madras, lb.	1.03	@	1.05
Logwood extract, 51°, lb.	.22	@	.27
Madder, Dutch, lb.	.21	@	.22
Methyl, violet, lb.	6.00	@	9.00
Methylene, technical, lb.	7.00	@	10.00
Prussian blue, soluble, lb.	1.15	@	1.25
Sulphur, black, lb.	1.30	@	1.50
Sulphur, brown, lb.	.45	@	.50
Zinc dust, prime to heavy, lb.	.25	@	.30
Zinc oxide, American, lb.	.11	@	.12
Zinc sulphate, lb.	.06	@	.07

ESSENTIAL OILS.

Almonds, bitter, lb.	\$ 12.50	@	14.00
Amber, crude, lb.	1.15	@	1.25
Anise, technical, lb.	1.00	@	1.10
Camphor, Japanese, 72 lb. cans, lb.	.16	@	.20
Cinnamon, lb.	19.00	@	20.00
Clove, lb.	1.20	@	1.25
Cubeb, lb.	3.15	@	3.25
Ginger, lb.	7.75	@	8.00
Limes, distilled, lb.	2.75	@	3.00
Pennyroyal, prime, American, lb.	1.65	@	1.85
Peppermint, prime, American, lb.	2.20	@	2.30
Spearmint, oz.	1.75	@	1.85
Wintergreen, synthetic, oz.	1.20	@	
Wormwood, oz.	2.85	@	3.00

FERTILIZER MATERIALS.

Ammonium sulphate, 100 lbs.	\$ 4.00	@	
Blood, dried, N. Y., 100 lbs.	3.70	@	
Bone black, sugar discard, ton	27.00	@	30.00
Bone black, old discard, ton	18.00	@	20.00
Phosphate, acid, per unit	.30	@	.36
Sulphate of potash, 90%, ton		@	3.00
Tankage, Chicago, 100 lbs.	3.30	@	

OILS.

Castor oil, No. 3 bbls., lb.	\$.13 ¹ / ₂	@	
Corn oil, crude, 100 lbs.	12.25	@	12.35
Corn oil, refined, 100 lbs.	13.00	@	13.05
Cylinder oil, light filtered, gal.	.26	@	.30
Cylinder oil, dark filtered, gal.	.19	@	.20
Fusel oil, refined, gal.	6.00	@	6.25
Linseed oil, car lots, gal.	.82	@	
Menhaden oil, crude, Southern, gal.		@	
Naphtha, auto, 68@72°, gal.	.37 ¹ / ₂	@	.36 ¹ / ₂
Paraffine oil, high viscosity, gal.	.29 ¹ / ₂	@	.30
Soya oil in bbls., lb.	.11 ¹ / ₂	@	.11 ³ / ₄
Spindle oil, No. 1, gal.		@	
Spindle oil, 20 gravity, gal.	.17	@	.18
Tar oil, commercial, gal.	.22	@	.23
Turpentine, gal.		@	

WAXES, ETC.

Beeswax, ordinary, pure, lb.	\$.32	@	.36
Ceresin wax, yellow, lb.	.16	@	.26
Ceresin wax, white, lb.	.25	@	.35
Japan wax, lb.	.14 ¹ / ₂	@	.15
Paraffine, crude, 124-126 mp., lb.	.05 ¹ / ₄	@	.05 ³ / ₄
Pitch, pine, first grade, bbl.	4.75	@	
Rosin, B grade, N. Y., bbl.	6.75	@	
Stearic acid, lb.	.12 ¹ / ₂	@	.17 ¹ / ₂
Tar, retort, bbl.	8.00	@	8.25

NOTES OF CHEMICAL AND ALLIED INDUSTRIES.

Air Products.—Plans are being prepared by the Linde Air Products Co., W. F. Barrett, Works' manager, 42nd St. Bldg., New York City, for factory buildings to be erected in the Central Manufacturing District, Chicago.

Alloys.—The U. S. Alloys, Inc., Buffalo, N. Y., has purchased a 10-acre site in Unit City, will erect a plant for the manufacture of alloys used in the production of steel.

Aluminum.—The United Aluminum & Smelting Co., New Haven, Conn., proposes the erection of an aluminum plant, to include five buildings, the largest to be 100x200 ft.

Chemical.—Good Chemical Co., of Basic City, Va., has been incorporated with a capital stock of \$100,000. L. M. Good is president and J. R. Swank, secretary.

Chemicals.—A chemical plant has been established at South Milwaukee by the Industrial Chemical Co., 200 Pleasant St., Milwaukee, Wis.

Chemicals.—The Kalbfleish Corp., C. D. McCollister, general manager, 31 Union Sq., New York City, will expend \$200,000 for erection of building and for equipment for plant at Chattanooga, Tenn., for manufacture of alum, sulphate and aluminum, etc.

Chemicals.—The Roessler & Hasslacher Chemical Co., Perth Amboy, N. J., proposes the erection of a \$1,000,000 plant near Charleston, W. Va.

Chemicals.—The Standard Chemical Co., Tacoma, Wash., proposes to double the capacity of its plant.

Chemicals.—Stauffer Chemical Co., New York City, contemplates erection of a plant at Manchester, Tex., for manufacture of chemicals and fertilizer material.

Chemicals.—The Sunshine Chemical Co., St. Louis, Mo., has been incorporated with a capital stock of \$10,000 and proposes to do a general chemical manufacturing business. D. H. Isch and Henry C. Henley are interested.

Chemicals.—The West Virginia Waste Wood Chemical Co., has been incorporated with a capital stock of \$300,000. Company has offices at 17 Battery Pl., New York City. J. E. Stevens is treasurer.

Coke.—The Semet-Solvay Co., which has plants at Ensley and Holt, Ala., has purchased 7,300 acres of coal land in Tuscaloosa County, and is said to contemplate erection of by-product plants.

Cotton Seed Products.—The Poe Cotton Seed Products Co., Memphis, Tenn., has been incorpo-

rated with a capital stock of \$100,000, and proposes to manufacture cotton seed products. H. F. Poe, Jr., Robert Wilson and W. M. Swift are incorporators.

Dyes.—Steps are being taken to organize the Kentucky Coal Products Co., of Clay City, Ky., to engage in manufacture of dyes. A. A. Laurie is interested.

Electrolytic.—Construction work is under way on a 2-story \$25,000 factory at Buffalo, N. Y., for the Commercial Electrolytic Corp., Buffalo, N. Y.

Explosives.—The E. I. Du Pont de Nemours Co., Wilmington, Del., has purchased a 40-acre site at Wallace, Idaho, and is reported contemplates establishment of an explosives' plant there.

Fabrikoid.—Work is under way on the erection of a \$250,000 plant at New Toronto, Ont., for the Dupont Fabrikoid Co., Dufferin St., Toronto.

Hydrogen Dioxide.—The Commercial Electrolytic Corp., Buffalo, N. Y., will erect a plant for the manufacture of hydrogen dioxide.

Lime Products.—The Tacoma Lime Products & Fertilizer Co., Tacoma, Wash., has been incorporated with a capital stock of \$100,000 by J. B. Anger, I. Carpenter and L. G. Stayton.

Nickel.—It is understood that the British-American Nickel Co., will start work soon on the erection of a refinery in the Welland, Ont., district. E. R. Wood and James P. Dunn, London, Ont., are interested.

Nickel.—The Foundation Co., Montreal, Que., is preparing to begin work on the construction of the \$5,000,000 refinery at Port Colborne, Ont., for the International Nickel Corp.

Paint.—Sherwin, Williams Co., paint manufacturer, 60 Canal St., Cleveland, O., have awarded a contract for the erection of four chemical buildings and power house at Chicago.

Paper.—The Atlantic Paper & Pulp Co., has been organized with a capitalization of \$1,000,000 and proposes to construct a plant at Port Wentworth, Ga., to have a capacity of 50 tons of pulp daily. Cost will be about \$500,000. I. H. Fetty, Savannah, Ga., is president.

Paper.—The Atlantic Paper & Pulp Co., Savannah, Ga., proposes the establishment of 50-ton per day paper pulp mill.

Paper.—The C. P. Boland Co., Troy, N. Y., has been awarded the contract for the erection of a \$100,000 paper manufacturing plant at Cohoes, N. Y., for the Frank Gilbert Paper Co.

Paper.—Colonial Pulp & Paper Mills, Ltd., Quatsino Sound, Canada, proposes to erect a sulphite mill of 120-ton per day capacity.

Paper.—Filer Fibre Co., P. H. Schnerback, manager, proposes erection of sulphite paper mill at Filer City, Mich.

Paper.—The Hattiesburg Pulp & Paper Co., Hattiesburg, Miss., incorporated recently with \$1,500,000 capital stock has plans under way for a plant. Friend & Webber, New Orleans, La., are the engineers. G. H. Wood, Fort Dearborn Bank Bldg., Chicago, Ill., is interested.

Paper.—Plans are being prepared for a hydro-electric plant and paper mill to be erected for the Flambeau Paper Co., Park Falls, Wis., at a cost of \$125,000. Guy Wilds is secretary. T. W. Orbison, Appleton, Wis., is engineer.

Paper.—The John Strange Paper Co., Neenah, Wis., has purchased the property of the Wisconsin Graphite Co. and will establish a paper mill. A new dam and hydro-electric plant is to be built near Stevens Point, Wis.

Paper.—Sugar By-Products Co., New Siberia, La., will install equipment for a paper mill, also for manufacture of cellulose, pulp, alcohol, etc., from sugar mill waste. The company has a capital stock of \$5,000,000. Mark W. Marsden, Widener Bldg., Philadelphia, Pa., is president.

Paper.—Plans are being prepared by the Union Bag & Paper Co., Bakers Falls, N. Y., for the erection of a 4-story paper mill.

Paper.—The Wheat Paper Co., Elkhart, Ind., will erect new fire proof buildings to replace the plant at Petoskey, Mich., recently damaged by fire.

Paper.—The Abitibi Power & Paper Company, Montreal, Que., will double the capacity of its paper plant, giving it an output of news print of about 400 tons a day.

Paper.—The International Land & Lumber Company, Ottawa, proposes to erect a 100-ton pulp mill on the Ashuapmouch River in the Lake St. John district. J. L. Bate, R. N. Bate and Thomas Asquith, all of Ottawa, are interested.

Paper.—The Manitoba Power, Pulp & Paper Company has had plans prepared for its plant to be erected at Grand Rapids on the Saskatchewan River. It will include a sawmill, paper factory, pulp mill and hydroelectric power plant. The capacity of the pulp and paper mills will be 100 tons per day. The whole scheme will represent an outlay of \$2,000,000. D. R. McDonald, Winnipeg, Man., is the promoter.

Paper Pulp.—The Great Southern Lumber Co., W. H. Sullivan, general manager, Bogalusa, La.,

will expend \$800,000 for construction and equipment of 60-ton pulp mill at 100-ton container liner plant.

Phosphate.—The phosphate manufacturing plant of the I. P. Thomas & Sons Co., Billingsport, N. J., destroyed by fire last month with a loss of \$100,000, will be rebuilt. H. H. Lippincott, Riverton, N. J., is president.

Portland Cement.—Arrangements are being made for the completion of the plant at San Juan, Cal., for the Old Mission Portland Cement Co. The plant will have a capacity of 2,000 bbls. per day.

Radium.—The U. S. Radium Works, Sellersville, Pa., is enlarging its plant.

Refinery.—Consumers Refinery Co., Oklahoma City, Okla., will establish a \$250,000 plant. A. D. Lloyd, Skervin Hotel, Oklahoma City, is the engineer.

Soap.—Geo. A. Fuller Co., Chicago, Ill., has been awarded contract for erection of an \$800,000 plant at Chicago, for the Jas. S. Kirk Soap Co.

Soda Pulp.—Construction work is under way on a \$500,000 plant for the Kingsport Pulp Corp., Kingsport, Tenn. Plant will have a capacity of 50 tons of soda pulp per day. Geo. F. Hardry, 209 Broadway, New York City, is the architect.

Sugar.—Savannah Sugar Refining Co., Savannah, Ga., has construction under way on a plant on the Savannah River to have a daily capacity of 1,000,000 lbs. raw sugar. Westinghouse, Church, Kerr & Co., 37 Wall St., New York City are the engineers and contractors.

Sulphuric Acid.—Michigan Sulphur & Oil Co., Orla, Tex., is considering installing machinery for manufacture of sulphuric acid. Wm. A. Doyle is manager.

Tannery.—Plans are under way for erection of two buildings to replace finishing department of tannery of Hans Rees' Sons at Asheville, N. C. One building will be 320 ft. long, the other 290 ft.

Tannery.—Plans are in progress for alterations to tannery of Pfister & Vogel Leather Co., Milwaukee, Wis.

Tar.—The Lewis Co., Chicago, Ill., will erect a tar by-product plant at Canal Dover, O., to refine tar from the coke plant of the Dover By-Product Co.

Wood Acid.—The Carolina Wood Acid Co., of Statesville, N. C., has been incorporated with a capital stock of \$75,000. W. E. Webb, J. B. Foster and J. C. McClure are the incorporators.

Burmese Myrabolans as a Tanning Material.

According to the Indian Trade Journal of Sept. 15, a report on the Burmese myrabolans or "pangia" fruits as a tanning material, prepared by the chemical adviser to the Forest Research Institute, states that the Burmese myrabolans are different from the Indian Chebulic myrabolans in points of tannin and non-tannin contents and color. In the air-dried Burmese material the tannin varies from 16 to 32 per cent; the general average may thus be taken to be 20-25 per cent, which is about half the tannin content of the Indian myrabolans. The nontannin ranges from 25 to 34 per cent, and the general average may be taken to be 27-30 per cent, which is three times that of the Indian myrabolans. The color is high. The maximum red and yellow recorded for the Indian myrabolans is 2.5 red and 7.4 yellow, while the Burmese myrabolans in general have 4.9 red and 18.35 yellow. The excess of nontannin is a disadvantage, and all tanning materials having nontannins in excess must be classed as somewhat inferior, though in practice they give fairly good results. To form some opinion as to the actual tanning properties of the Burmese myrabolans experiments were undertaken, which disclosed that leather made with this material alone is spongy and tough like the leather produced by Indian myrabolans, that the Burmese fruits can be used in the preparation of butts for making army boots and shoes and also for making black uppers of inferior quality, and that they will be useful in conjunction with babul bark for making sole leather.

Mineral Products of the United States in 1915.

The value of the mineral production of the United States in 1915, according to preliminary figures compiled by the United States Geological Survey, was approximately \$2,373,000,000, a gain of \$258,000,000, or more than 12 per cent over 1914. The value for 1915 has been exceeded but once—in 1913—when a total of \$2,439,000,000 was recorded.

Metallic products.—The metallic products reached the greatest value ever recorded, having advanced from \$691,000,000 in 1914 to \$987,500,000 in 1915—a gain of nearly 43 per cent. The metals contributing most largely to this increase, their combined gains being 91 per cent of the total, are as follows: Pig iron, increase, \$102,630,000, or 34 per cent; copper, \$89,930,000, or 50 per cent; and zinc, \$78,580,000, or 224 per cent.

Nonmetallic products.—The value of the nonmetallic products in 1915 has been exceeded in 1913 and 1914 only, showing in 1915 a decrease of less than 3 per cent from the preceding year. The figures for 1914 and 1915 are \$1,423,000,000 and \$1,385,000,000, respectively. The final figures for the value of the nonmetallic products in 1915 may be somewhat increased over the preliminary figures given.

The mining activities and output reported for the

six months just ended show that 1916 promises to be a record-breaking year in the value of mineral products.

Russian Paper Making Industry.

A recent issue of the *British Paper Trade Journal* states that the improvement in the conditions of the Russian paper-making industry, which has latterly been noted, is maintained, but there are still complaints of the shortage of raw materials, chemicals, etc. The situation, however, is considered to be slowly but surely readjusting itself, and hopes are entertained that before long something approaching to normal conditions will prevail.

A considerable increase in the export of pitprops, pulp wood, etc., from Archangel during 1915 is reported, the quantity being 34,006 cubic sazhen, compared with 21,200 cubic sazhen in 1914 (11,648,755 cubic feet in 1915 and 7,285,696 cubic feet in 1914).

Developments are taking place in the Siberian paper industry. In addition to the construction of the Gorochoff paper factory, a similar enterprise is being organized for Krasnoyarsk or Irkutsk; the paper-making works of I. E. Yatess is being formed into a company; the Volojod and Tver district council are contemplating the erection of paper works in the northern timber areas of Russia and Siberia, near the town of Taiga. According to a report by M. V. I. Minaieff, presented to the Society of Engineers of Tomsk, the annual consumption of paper in Siberia amounts to 2,000,000 or 3,000,000 poods (36,000 or 54,000 short tons) and is increasing. As there should be no difficulty in regard to the provision of rags and mechanical and chemical pulp from local sources, the prospects for the paper-making industry are very promising.

WANTED—3 chemists and metallurgists—iron, steel and similar work; \$100-\$175 per month. H. H. Harrison & Co., Association Bldg., Chicago.

CHEMISTS and metallurgists with industrial and commercial experience. Several good positions open paying between \$60-\$125. The Engineering Agency, Inc. (23rd successful year), 1662 Monadnock Bldg., Chicago, Ill.

WANTED—"Research Chemist" to install and operate laboratory, investigating principally properties of Portland cement and methods of improving manufacture. This position is one in which the individual inclination for investigational work will be given every encouragement. Address Box 568, care of Chemical Engineer and Manufacturer.

WANTED—Electro-chemical engineer, thoroughly familiar with various processes in electro-chemical industries, and able to apply electrical apparatus thereto. Write fully. H. H. Harrison & Co., Association Bldg., Chicago.

WANTED—Man thoroughly familiar with the manufacture of optical glass. European experience essential. Right salary to right man. H. H. Harrison & Co., Association Bldg., Chicago, Ill.

THE CHEMICAL ENGINEER

VOL. XXIV.

DECEMBER---JANUARY, 1917

No. 6

Published Monthly by the

McCready Publishing Company.

ROBERT H. MCCREADY, President

DAVID R. PERAZZO, Treasurer.

118 East 28th Street, New York.

LAURANCE T. CLARK, Editor

Entered as Second Class Matter at the Post Office at New York, N. Y., under the Act of March 3d, 1879.

Subscription—United States, Cuba and Mexico, \$2.00;
Canada, \$2.50; other countries, \$3.00.
Single Copies, 25c.

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THIS ISSUE.

Owing to a combination of circumstances, this issue of THE CHEMICAL ENGINEER has been so delayed in publication that it has been decided to combine two numbers in one. All subscriptions will be extended correspondingly, so that every yearly subscriber will receive twelve complete issues.

THE CHEMICAL ENGINEER

In order to more clearly indicate the field covered, and also for the sake of that brevity which is an essential part of true economy, the title of this periodical has been changed from the CHEMICAL ENGINEER AND MANUFACTURER to THE CHEMICAL ENGINEER, which was the title used until about the middle of last year.

The importance of the chemist in the industrial world is becoming more and more appreciated everywhere. The scope of his work is broadening with remarkable rapidity; he calls upon his knowledge and his resourcefulness lead him daily into new and hitherto unsuspected fields.

There is no doubt whatsoever that this country is approaching a period in its history when efficiency and economy of manufacture will represent the cornerstone in the structure of success. Natural resources, geographical advantages, self-sufficiency—these things will fade into the background. We will come into competition with a new world—a world chastened by misfortune, tempered in the fierce fires of warfare, trained by the most exacting experience. When this war is over, America will be the Old World and Europe will be the New.

To the Industrial Chemists of America, with their new problems, their new responsibilities, and their new opportunities, THE CHEMICAL ENGINEER will be dedicated. It will stand squarely behind the American Chemist in his work for the development of American Industries.

The Utilization of By-Products from the Manufacture of Coke*

BY C. B. ATWATER.†

At a recent meeting of the American Chemical Society in New York for the award of the medal established in honor of Sir Henry Perkin (himself one of the greatest investigators in the field of coal by-products) to Dr. Leo Baekeland, a distinguished worker in the same fertile field, one of the speakers, referring to the coal tar chemical industry, said that it was not so much the relatively few millions of investment, but that with its hundreds of typical reactions, its thousands of substances, and its profound study of the actual spacial relation of atoms in the molecule, scientifically its development represented one of the greatest intellectual achievements of the race. It seems to me that this statement can be well made to cover the whole branch of coal by-products. I know of no substance whose uses so fill the scope of our engineering, manufacturing, chemical, domestic and social needs as do those of coal. Its consumption per capita is fairly taken as the measure of a nation's civilization; its possession is the guarantee of a nation's future; in the development of its possibilities we appear to have only crossed the threshold; in the application of the possibilities we have demonstrated, we are certainly far behind what might be done. While it is probably presumptuous for an outsider to attempt to tell the dwellers of the "Coal City" anything about coal that they do not already know, there may perhaps be some justification on the score that from a more distant point of view things may be seen less accurately but more nearly in their proper general proportions; and furthermore, that in the case of those who have no coal, the appreciation of its value is not dulled by possession.

If there be any one who doubts that great natural law of the indestructibility of matter, certainly consideration of coal and its by-products should convince him. We do not know how hot the sun was in the forests of the Coal Age; we do not know whether continuous thunder storms helped in nitrogen fixation; we do not know the color of the tropical vegetation, the odor of its blossoms, nor the taste of its fruits; whether they were poisonous or healthful, whether they grew slowly year by year or shot up over night as in fairy tales; but we do know that, buried deep in the earth, lost forever according to human standards, through centuries, we receive again the sun's heat and light and through the glowing furnace and in response to the chemist's skill we again see those colors, smell the odors, and grow sick or recover from the drugs. We may even taste those flavors and eat the fruits, or if not exactly them, at least some synthetic product so much like them that the ordinary man cannot tell the difference.

Thirty-five years ago William Siemens, a man of prophetic vision, speaking of the prospects he saw in the economical treatment of coal, said: "I am bold enough to say that raw coal should not be used as fuel for any purpose whatsoever, and that the first step toward the judicious and economic production of heat is the gas-retort or gas-producer, in which coal is converted either entirely into gas, or into gas and coke, as is the case at our ordinary gas works." After thirty-five years we have made some progress and it seems now as though his vision were on the way to be fulfilled.

The distillation of coal is practiced in three general types of apparatus, namely, the coal gas retort, the beehive coke oven, and the by-product coke oven; therefore, the industries dealing with the products of coal distillation are based on the operation of these three agencies. The coal gas retort produces primarily coal gas for use as an illuminating gas and also as by-products, coke, tar and ammonia, and in some instances benzol and cyanides. The by-product coke oven produces coke as its main product and as by-products, gas, which may be used for illumination, tar, ammonia, benzol and cyanides. The beehive oven produces only coke and should not perhaps be included in this catalogue except that it comes under the general classification and is of interest as occupying the industrial field, we may reasonably expect will ultimately be pre-empted by the by-product coke oven. It is, as it were, a measure of our immediate possibilities. I do not include the gas producer in this category because coal is not, strictly speaking, distilled destructively in this process, as air enough is introduced to partly consume it and transform it into carbonic oxide, which is attended with practically the destruction of the by-products of distillation except in the case of the recovery gas producers, where ammonia and a small amount of tar are recovered.

The development of the industries based upon the distillation of coal may be said in this country to have actually depended upon the introduction of the by-product coke oven. This statement will, I think, be justified by an examination of the conditions. It would not be true of Great Britain, to any such extent at least. The great extent to which coal gas is manufactured in England, and has been for many years, had supplied the materials for the chemical industries to work with, aided by the limited territory, which facilitates the assembling of supplies from different works.

This statement would be, however, true of Germany, where coal gas is not so widely used and where the introduction of the by-product coke oven began at an earlier date. In the United States the coal gas industry has long been in existence, but has been, as it were, diluted so much by the immense area of our country and the preponderance of carburetted water gas that

*From the Proceedings, Engineers Society of Western Pennsylvania.

†Manager, Agricultural Department, The Barrett Company, New York.

until the advent of the by-product coke oven the supplies of raw material did not encourage the development of an extensive industry based on the products of coal.

In order to arrive at the relative importance of these three methods of destructive distillation, I would give the following figures, calculated from the latest reports of the United States Geological Survey:

	Tons.	Per Cent.
Coal distilled in by-product coke ovens	17,100,000	23
Coal distilled in coal gas retorts.....	4,000,000	6
Coal distilled in beehive coke ovens...	52,100,000	71
Total coal distilled.....	32,200,000	

As will be seen from these figures, the by-product coke oven is about four times as great as the coal gas retort, but both combined fall far short of the total of the beehive coke oven. These figures indicate that a large amount of by-products are recovered. They also show that a still larger amount will ultimately be available and must be reckoned with in our industrial calculations.

The primary products of the distillation of coal, as I have already stated, are coke, gas, tar, ammonia, benzol, and cyanides. To simplify matters I will take them up in order.

COKE

The nature and varieties of coke are, I presume, well known to you. Its main use is, of course, in the smelting of pig iron, for which approximately a ton must be manufactured for each ton of pig iron produced, although the actual consumption at the furnace is a little below this amount. For this purpose metallurgical coke is required, that is to say, coke having a strong cellular structure and reasonably low in sulphur, phosphorus and ash. Metallurgical coke is also used for remelting pig iron in the foundry cupola.

The softer coke produced by the coal gas retort has found ready consumption for ordinary fuel purposes. Aside from its lack of strength and liability to make breeze, it is better fitted for ordinary fuel purposes than the harder metallurgical coke, as it is not so difficult to ignite.

A considerable trade is being built up in certain districts in domestic coke, which is usually the by-product article crushed and sized and distributed in the usual manner. It has been found very satisfactory for all fuel purposes where a little attention is given to its properties, as distinct from anthracite or bituminous coal. It is quite probable that the future will see considerable extension in this direction as the other products of coal distillation become more desired and justify investment in coking plants. In this connection it may be remarked that we are informed that large quantities of coke are now consumed in Germany in place of coal, it being desirable to operate their by-product coke ovens for the production of ammonia and of benzol, toluol, etc., although the coke is not specially required.

AMMONIA

The usual way of obtaining ammonia in the by-product coke oven system has until recently been by washing the gas with water, which, having a strong affinity for ammonia, absorbed it, the product being weak ammonia liquor. This ammonia liquor was distilled by steam in a column to form crude concentrated liquor or led into the sulphuric acid saturator, where by combination with sulphuric acid, sulphate of ammonia was formed. The sulphate was then dipped out of the saturating vessel, either by hand power or by air lift, dried in a centrifugal dryer and stored for shipping as the finished sulphate. Recent improvements in coke oven by-product apparatus have modified this method to the extent that the coke oven gas, after being freed from tar, is led directly to the saturating boxes and by the combination of the ammonia gas with the sulphuric acid, sulphate of ammonia is formed directly without the intervention of any washing water. This is known as the semi-direct process and produces an excellent quality of ammonia sulphate. In the plants that are so far in operation in this country, as those at Joliet, Gary and elsewhere, where ovens of the Koppers type are used, a certain amount of weak ammonia liquor is also produced, due to the cooling of the gas before passing through the saturator in order to remove the tar. With the tar a certain amount of ammonia liquor comes down. This ammonia liquor is usually in the form of the fixed salts—chloride, sulphate, sulphite, thiosulphate and ferrocyanide, and must be freed by the addition of lime or other alkali and distilled in the usual column still. The ammonia vapor so obtained is either returned to the gas main at a point just before the gas enters the ammonia saturator, or it can be kept apart and used for making ammonia liquor.

These two products, crude concentrated ammonia liquor and ammonium sulphate, are the primary ammonia products. From them the secondary products are manufactured. These comprise principally anhydrous ammonia and aqua ammonia, which are used in refrigeration and chemical manufacture; ammonium carbonate and ammonium bi-carbonate, which are used as leavening agents in baking; ammonium nitrate, which is used in the manufacture of explosives; ammonium chloride, more generally known as sal ammoniac, which is largely used in the manufacture of electric batteries and for various technical purposes. The most important of the products, as far as quantity goes, is ammonium sulphate. This is an important carrier of nitrogen for agricultural use and is a component of most mixed fertilizers produced in this country. It is generally accepted as one of the principal forms of nitrogen in all agricultural countries and is shipped all over the world for this purpose.

Until the breaking out of the war Germany was the greatest producer of sulphate of ammonia of all the countries, having surpassed the English production two or three years ago. The total German output for the year 1913 was 548,000 tons, England's maximum pro-

duction being 432,000 tons, reckoning all forms of ammonia produced as the sulphate. The United States stands third in this rank, having produced 220,000 tons in the year 1915, the largest production recorded to date. Chemically pure sulphate of ammonia will contain about 25.8 per cent NH_3 and as ordinarily produced it contains 25 per cent or over, this being a high degree of purity for a commercial article produced in large quantities. It is of a dry, granular consistency and lends itself well to use in fertilizer mixtures. It can also be dried and ground and used as a direct application for top dressing growing crops. It is the most immediately available source of chemically combined nitrogen that the country has at its disposal and is one of our most valuable natural resources from this point of view. It is estimated that the nitrogen stored up in an acre of the ordinary four-foot vein of bituminous coal is sufficient to fertilize the acre of land above that coal liberally for a period of 3,840 years. Unfortunately, all the nitrogen contained in the coal is not available for recovery, a part being lost because of the necessary amount of coal left in the mines and a further portion being lost in the conversion of the coal to coke and the recovery of ammonia. Allowing for all these losses, however, there still remains enough nitrogen recoverable in the form of ammonia sulphate to maintain the fertility of an acre for the period of 640 years. With these figures in mind we can appreciate the importance of the waste that is now going on in the carbonization of coal in the beehive coke oven, and furthermore, the great economic waste that takes place in the consumption of bituminous coal in the ordinary manner.

The question of ammonia recovery has taken on new importance because of the conditions developed by the war, and the imperative need for nitric acid in warfare. As you are all probably aware, nitric acid is the *sine qua non* in the making of modern explosives.

A number of years ago the great German chemist, Dr. Ostwald, discovered a method of oxidizing ammonia to form nitric acid. The process was a simple one, involving the passage of ammonia gas together with sufficient air through a heated tube in the presence of a platinum catalyst. This process was never developed to any extent commercially, as enough nitric acid was always to be obtained from Chilean nitrate of soda, and at a relatively low cost, so that there seemed to be no financial inducement. The matter, therefore, lay dormant.

On the outbreak of the war Germany was confronted with a critical condition in her nitric acid supply. Her annual imports of nitrate, amounting to 850,000 tons, were cut off. Not only was it necessary to supply its place in agriculture and in chemical manufacture, but a new demand had arisen for nitric acid for explosives. So far as information has reached us in this country, Germany has turned to the Ostwald process, or some development of it, and is now obtaining her nitric acid from ammonia by oxidation. We are told that she is now consuming from 250,000 to

300,000 tons of nitric acid per year for explosives, of which only 10,000 tons is obtained by the arc process of nitrogen fixation, the balance being obtained from ammonia derived from calcium cyanamid or produced synthetically by the Haber process.

Germany has for years recovered all the ammonia available in coke production. Therefore no room existed for expansion in that direction. But in the United States we are annually wasting over five hundred thousand tons of sulphate of ammonia that is produced in beehive coke manufacture but not recovered. If half of this were recovered we would have a sufficient addition to our present supply to equal the present German consumption for munition purposes, as above stated.

The development of the arc process for the direct recovery of nitrogen from the air, as done in Norway, offers many difficulties in this country. Chief among them is the lack of large water powers lying within our borders where power in large quantities could be produced at a price low enough to make continuous operation feasible in time of peace, even with Government support.

The production of calcium cyanamid, as done at Niagara Falls, is more attractive, but Niagara Falls is on our border, open to attack. Moreover, from cyanamid we obtain only ammonia, which we can more easily obtain from coal. The retort coke oven plants lie at well scattered points in the interior, and are not open to enemy attack.

It seems to me that the point on which stress should be laid, and on which Government support should be elicited, is in the development of the process for ammonia oxidation. With that cleared away our own natural resources would become available.

GAS.

The gas produced from the distillation of coal in the by-product coke oven is essentially the same as ordinary illuminating gas. A fair average analysis of such gas is as follows:

	Per cent.
Hydrocarbons	5.8
Methane	40.8
Hydrogen	37.6
Carbon Monoxide	5.6
Carbon Dioxide	3.7
Oxygen	.4
Nitrogen	6.1
	100.0

Generally speaking, the gas will run from 600 to 700 B. t. u. per cu. ft. and will have from 14 to 16 candle power. It is capable of being used for all the purposes to which ordinary city gas is put, that is to say, not only may it be used in ordinary gas burners, stoves, heating ovens, etc., but it can be used for power in gas engines and can be transported long distances under pressure. Its illuminating value is due principally to the benzol and other higher hydrocarbons which it contains. In order to obtain the maximum illuminating value in coke oven gas a method of operation is frequently resorted

to, which is known as the division of gases. The first portion of the gas given off from an oven of coke is, of course, the richest in illuminating as well as in heat value. Therefore, it may be readily understood that if the first portion of the gas from each oven is kept by itself in one system of mains and the later, leaner portion of the gas carried through a separate system of mains, the first gas will be much more valuable for general city purposes than the leaner gas. It is understood, of course, that the present system of heating the coke ovens is with a portion of their own gas. For this purpose the illuminants are by no means necessary, so the oven heating suffers no appreciable loss and the disposable gas is afforded a decided gain where this principle of the division of gases is practiced. The two gases remain distinct all the way through the condensing and scrubbing processes and the clean gas comes from the condensing house in two separate mains. One is led back to the ovens for firing them, the other is piped away for whatever purpose it may be desired. Roughly speaking, the proportion of gas under modern conditions is about half and half; that is to say, of the 10,000 cu. ft. of gas which a net ton of coal is usually supposed to deliver, about 5,000 feet is used for heating the ovens and 5,000 feet is disposable. With the shortened coking time that now prevails a greater proportion of gas is disposable, only about 4,000 feet being necessary to heat the ovens in some plants. Usually the separation of the gases is made at the oven, proportioning the two quantities as nearly as may be by manipulating the valves, more rich gas being taken, if anything, than is necessary. If more oven heating gas is needed the rich gas can be by-passed in the fuel gas holder.

This plan of increasing the strength of the rich gas by taking the unessential portions from the poor gas has been carried even further where benzol recovery is practiced, by scrubbing the lean gas to obtain its benzol, and adding this benzol as an enricher to the rich gas; in fact, where benzol is recovered, it has been found expedient to remove all the benzol from both gases and deprive them of their troublesome naphthalene, and thus greatly facilitate the transmission of the gas in cold weather. After the benzol has been purified it is returned to the rich portion of the gas and a better and cleaner gas is thus obtained.

The usual type of condensing house for treating coke oven gas does not include purifiers to remove the sulphur. For the portion of gas used in heating the ovens the presence of sulphur is of no moment, and if it is possible to dispose of the surplus gas for usual city purposes, this in most cases has been done through the existing gas company, and the purification from sulphur is attended to by them. In a number of instances the capacity of the district where the coke ovens are located to consume illuminating gas is far behind the production of the coke ovens, and other uses must necessarily be found. In some cases this

has been done in the open hearth steel works, in the various heating furnaces, soaking pits, etc., accessory to steel mills, or in ordinary boiler firing. A much more desirable and economical use is, of course, in the internal combustion engine, where a great economy in the production of power may be obtained.

Although the by-product coke oven consumes nearly one-half of its own gas production, the surplus gas produced is usually very large in quantity because of the great amount of coal treated. The relation between the surplus gas production at such a plant and the consuming capacity of the ordinary sized town is not generally appreciated. A town, say, of 50,000 inhabitants, where gas is generally used, may possibly consume 5,000 cu. ft. per inhabitant per year, or about three-quarters of a million feet per day. A blast furnace producing 100 tons of pig iron per day would require a by-product coke oven plant of this size, and while a furnace of this capacity would be all right as far as it went, it would be something like the Ford among automobiles—good enough, but not anything to brag about. It will, of course, be recognized that it is a great advantage to by-product coke oven operation to be able to sell its gas for city consumption, where the price ranges from 60c. to \$1.00 per thousand to the ultimate consumer, rather than for purely fuel purposes in competition with coal. This may be the better appreciated when it is explained that the value of coke oven gas is about four cents per thousand cubic foot when used in competition with coal at \$1.25 per ton for firing boilers, or where the coal is gasified in gas producers. Where more advantageous methods of disposal are available much higher prices may, of course, be obtained. (In fact, from a broad economical point of view, the use of such gas under steam boilers is wasteful and is a sacrifice of a high grade product to a low grade use.)

BENZOL.

I have already referred to the recovery of benzol from coke oven gas. This is, in fact, the main source of all the benzol produced, although coal tar is usually credited with containing the benzol, which forms the foundation of so large a portion of the coal tar chemical industry. This is also true of the products allied to benzol—the toluol and xylol. Crude benzol, as obtained by washing this coke oven gas, is in reality a mixture consisting principally of these three. The process of recovering the benzol consists in washing the gas with a heavy oil, usually derived from coal tar or petroleum "straw" oil, until this oil is charged with the crude benzol, when it is removed from the circulating system and distilled at such a temperature as to drive over the benzol and allied vapors without disturbing the original washing oil. This oil may then be cooled and returned to the circulating system. The type of washer used for this purpose does not differ in any essential particular from that used in washing the gas with water to obtain the ammonia, the principle

being to expose as large a surface of the washing oil as possible to the gas to facilitate absorption. The quantity of crude benzol contained in gas varies from two gallons per ton of coal carbonized to very much less than this, according to the volatile matter in the coal. The subsequent treatment of the crude benzol to separate it into its various fractions is carried out by fractional distillation between limited temperatures. Ninety per cent benzol, which is the usual commercial standard, is that product 90 per cent of which will distill over at 100 deg. Cent. or lower.

The production of benzol from coke oven gas has been extensively carried on in Germany and the large amounts of benzol so secured have been one of the main raw materials for their highly developed coal tar chemical industry. The surplus benzol was used as a motor fuel in place of gasoline, and under the present war conditions, benzol is the principal fuel for automobiles and similar engines.

Pure benzol is also the starting point for the manufacture of aniline oil and a wide range of dye stuffs, pharmaceuticals, etc., based on it. It is also important at present because from it pure phenol or carbolic acid can be synthetically produced. There is a great scarcity of phenol at present, as it is extensively used for making tri-nitro phenol or picric acid, an explosive, also for the peaceful use of making phonographic records.

The separation of the toluol from the crude benzol also supplies material for making tri-nitro toluol, a very important explosive used by the armies and navies of most nations in their shells, torpedoes, mines, etc.

The amount of benzol produced in the United States was very small until subsequent to the outbreak of the European war. If all the coal made into coke had been treated for benzol recovery, we would have had a production of about one hundred million gallons per year, on the moderate estimate of one and one-half gallons per ton of coal. It is stated on good authority, however, that the total recovery in 1913 was not more than four million five hundred thousand gallons, outside of that used for gas enrichment by the producer. The European war, however, not only cut us off from our foreign supplies of chemical and dye stuffs based on benzols, but immensely increased the demand for it because of the manufacture of war munitions in this country. Accordingly many benzol recovery plants have sprung into being, and this article hitherto, if not actually wasted, at least lavished on uses far below its potential value, is now in a fair way to come into its own. The Geological Survey in a recent report states that the output of benzol and light oils in 1915 was nearly 14,000,000 gallons and that with the completion of the new plants under construction the capacity will probably exceed 22,000,000 gallons per year. The price for refined has risen from 25c per gallon to 60c or upwards, while toluol, formerly in

limited demand at 30c per gallon, has risen to \$4.25 per gallon and upwards.

As benzol is an excellent motor fuel, it is quite probable that any surplus existing after the close of the war can be readily absorbed for this purpose, although we may well hope that the development of our chemical industries will afford an adequate and more remunerative market.

CYANIDES.

The presence of cyanogen in coal gas is generally attributed to the breaking down of ammonia in contact with hot coke or oven surfaces. Therefore, while the amount of cyanogen present depends originally on the amount of nitrogen in the coal, it has also an immediate relation to the heat of the coke oven or gas retort, in which the carbonization is carried on. High heats and exposure to hot surfaces encourage cyanide formation and low heats the opposite. The usual form in which cyanogen occurs is as hydrocyanic acid, HCN, thus



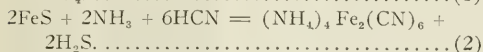
The actual amount of cyanogen in a gas is small. Tests have shown that of the original nitrogen of the coal, amounting to one or two per cent, only between one and two per cent appears as cyanogen. A gas containing 130 grains of cyanogen per cubic foot can be worked profitably, it is said, provided the amount of coal treated approximates 200 tons per day.

In the usual method of purifying coal gas, by the use of iron oxid, more or less of the cyanogen is removed. Under favorable conditions the spent oxid will be found to contain enough to warrant treatment. This is usually done by chemical manufacturing concerns so located as to get suitable oxid from several works near enough to avoid heavy freight charges. These works purchase the spent oxid on the basis of its prussian blue contents, and work it up, the final product being yellow prussate of potash, potassium ferrocyanide, or an equivalent form.

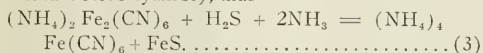
The complete removal of cyanogen from gas as a separate operation can be done in accordance with several different methods, as the Bueh, the Davis-Neill, Feld, etc., and is carried out on a commercial scale in a number of European gas plants. The Bueh process is perhaps the best known, and is employed at at least one of the two or three plants in operation in the United States, as well as at a number of European works. It consists primarily in washing the gas with a solution of ferrous sulphate, FeSO_4 . This is done by passing the gas through a gas washer of one of the usual types, using the sulphate of iron solution as the washing liquid. As the presence of ammonia in the gas is essential to the reaction, the point chosen is previous to the ammonia washers. It is also necessary that the gas be first freed from naphthalin by passing through a washer in which a suitable absorbing medium, an anthracene oil, creosote oil or water gas tar, is used. The gas

therefore passes through the naphthalin washer first, and then goes to the cyanide washer.

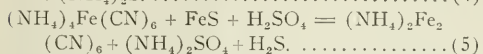
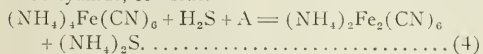
In the latter, the fresh sulphate of iron enters at one end and the gas at the other, the currents being opposed. The FeSO_4 reacts with the H_2S in the gas and iron sulphide, FeS , is formed. This in turn reacts with the CN and the NH_3 , forming ammonium ferro-ferro cyanide.



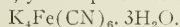
Some soluble $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$ is also formed (ammonium ferro-cyanide), thus



The sludge liquor from the washer is treated in a still and then neutralized with sulphuric acid. It then contains an insoluble double ferrocyanide of ammonia and iron, plus ammonium sulphate, ferrous sulphate and free acid. It is run to a filter press, and the sludge removed in the form of press cake, ammonium ferro-ferro cyanide, or "blue."



The final product is sold on its equivalent to potassium ferrocyanide, yellow prussiate of potash,



Under present conditions sodium ferrocyanide is made instead of potash, because of the high price of the latter.

TAR.

The human mind is eager for paradox. That is why it seizes on the contrast between black, ill-smelling, obnoxious tar and the many colored, highly refined and variously useful products made from it. The wonders of coal tar chemistry are on every lip, and nothing is too impossible to be readily credited if tar is the starting point.

I am sorry that I cannot go very far with you on this inviting road, and I am afraid that what I have to show you will be rather prosaic by contrast. Our American coal tar industry has not yet reached the "Bird of Paradise" stage.

The removal of tar from crude gas was long a sticking point in methods of condensation and is still a criterion of good operation. As the gas cools, tar is deposited very readily, but the last traces of tar are not so easily removed. This is usually effected by passing the gas through a scrubber in which it is finely divided, together with a reduction in temperature to about 80°Fahr. , the latter being deemed essential to success. The temperature reduction has, however, been avoided by the use of a scrubbing device in which a jet of tar acts on the gas, and causes the tar mist to gather into drops which readily separate out. Until

this difficulty was overcome the presence of tar in the gas prevented the adopting of direct saturation by which the ammonia is removed from the gas by passing through sulphuric acid, making sulphate of ammonia directly in place of washing with water and redistilling.

When coal is distilled in the gas retort or retort oven the lighter portions of the volatile matter in the coal go off as gas and heavier ones go off as tar. The dividing line seems to be about in the benzol-toluol-xylol series. Part of these go in the gas and part stay in the tar. It is not, however, a fixed line, but varies up and down according to circumstances. Nor is tar itself by any means a definite compound. Tars from different coals and more especially produced in different types of apparatus vary within wide limits. The more highly heated the surfaces over which the tar vapors pass on their way out of the retort, and the longer the exposure, the heavier the tar. The percentage of free carbon is a fair indication of its quality, as the amount of oils and bitumens are apt to vary with it. Generally speaking, coke oven tars are low in free carbon averaging around ten per cent, while gas-works tars are apt to be high, 25 to 30 per cent, and correspondingly lower in tar oils. Because of these variations and also because of the invariable presence of two or three or more per cent of water there are few if any purposes to which crude tar can successfully be put without preliminary treatment, except to burn as fuel.

Therefore, for whatever purpose the crude tar is to serve, it has to undergo the process of distillation and probably admixture with other tars to correct defects in composition.

The distillation of tar is carried out in steel plate stills of cylindrical form, these being set vertically in Europe, but usually horizontal in the United States. A standard type is of half-inch plate, nine feet in diameter and 20 feet long, holding about 10,000 gallons. These are set in brick work with a fire box beneath them, usually several stills in a battery. The vapor from the stills is led away through a goose-neck to a condensing coil, which is immersed in a tank of water, the temperature of which can be regulated. The separation of the distillation products is controlled by a thermometer placed in the goose-neck, cuts being made at certain specified points. For refined tar the removal of the water and a certain portion of the light oils is sufficient. Such refined tar is used in the saturation of felt for roofing, waterproofing and insulating purposes. In combination with soft pitch, saturated felt is built into a foundation or laid on a roof for waterproofing or roofing in successive layers.

It is also used in the manufacture of ready roofings, two ply, three ply and mineral surfaced. Another very important use of prepared tar is as good as a road application or binder. For this purpose several different grades are made, each suited to a special field. They range from a thin tar to what is really a soft pitch of 100° melting point.

When the distillation is to be carried out to the production of the various oils and pitch the separations are as follows in this country:

The first fraction is that which comes over below 200° Cent., or until the distillate sinks in water. This is called light oil or crude naphtha.

The second fraction comes over between 200° and 270° Cent. and is called middle or carbolie oil. The third fraction includes the oil above 270° until pitch of the required hardness remains in the still. It contains naphthaline and anthracin, and is known as heavy oil or creosote oil. It is extensively used in wood preservation under many and more or less complicated specifications.

The residue is pitch. In our American practice pitch varies greatly in hardness, the bulk of our production being the softer grades used for roofing, paving, waterproofing and preservative coatings. Some hard pitch for use in fuel briquettes and similar purposes is also made.

The proportion of these five preliminary products in tar varies with the tar, but is about as follows:

Light oil	0.5 to 3 per cent
Carbolie or middle oil	5.0 to 8 per cent
Creosote or heavy oil including anthracin oil	20 to 30 per cent
Pitch	60 to 75 per cent

I have already mentioned the various uses to which the crude products are put and will now run over

some of the products derived from them by further treatment, and their uses. I may say, here, that these cover a wide range and are by no means confined to dye stuffs and explosives.

LIGHT OIL.

From this benzol, toluol and xylol are obtained as already explained, and in addition a number of different solvent naphthas, also some phenol, creosol and naphthalin.

MIDDLE OR CARBOLIC OIL.

From this we obtain tar acids or crude creosols and crude naphthalin, also some creosote oil which is added to the heavy oil fraction.

From the first two we obtain phenol or carbolie acid, already referred to, a powerful antiseptic and disinfectant, also nitrophenol, the starting point for many dye stuffs, also trinitro-phenol or picric acid. This was used for a long time in medicine for the treatment of burns, as a textile dye and as an explosive in war. From the crude products we also obtain cresylic acid, and naphthalin, which is made into lumps, balls and flakes to keep moths out of woolen clothes. Naphthalin is also converted into nitronaphthalin, from which many dye stuffs are made.

HEAVY OIL.

In addition to the naphthalin which has already been referred to, heavy oil contains anthracin, from which in turn comes alizarin and anthraquinon, from both of which a wide series of dye stuffs is obtained.

New Aspects of Chemical Science*

By J. MERRITT MATTHEWS

The past two years have offered great inspiration both in thought and accomplishment to the American chemist. The past recent meeting of the chemical societies in this city, together with the elaborate Exposition of the Chemical Industries, has formed what might be termed the apotheosis of Technical Chemistry.

The American Chemical Society has heretofore confined its attention probably more to the consideration of pure chemistry of an academic character rather than to the industrial aspects of the science. This latter point of view has been left more to the technical societies. There has, however, been a more or less growing demand for an added emphasis to the features of applied chemistry. This demand has found its expression in the remarkable development of this journal so ably and successfully edited by Professor Whitaker. The general trend of our meetings has also shown the influence of this same leading force; the American chemist is evidently becoming vitally interested in the application of his science; it might almost be said that

he is seeking to bring it up from the state of an art to the true dignity of a science.

This growing tendency in our Society naturally leads to some philosophical reflections on the relations of technical chemistry and pure chemistry—the human relations of chemistry as distinguished from its purely academic features.

Technical chemistry must, of course, be considered as a branch of applied science, and as such more or less in opposition to "pure science." In using the term "pure science" it is my purpose to convey the meaning of science studied as an end and an ideal in itself; science that seeks for nothing beyond its own development, and having no ulterior motive than that of its own aggrandizement. Like virtue, it is its own reward; and like virtue, it also demands many sacrifices from its devotees. Its domains are vast; its treasures are countless; its follows are those to whom the lust of knowledge is the ambition of life. It is the science of the schools and the scholars, of the life-long student and the philosopher. Its wealth is not measured in money, but in the understanding of the phenomena of Nature.

*Chairman's address, Oct. 13, 1916, New York Section American Chemical Society, Chemists' Club.

It seeks after a knowledge of the laws of the world, and probes deeply into the mysteries of the universe; no fact is too humble for its recognition, nor too vast for its comprehension; no problem is too trifling for its attention, nor too sanctified for its solution. Its object is truth for the sake of truth alone; knowledge for the mere sake of gratifying the desire of knowing. The astronomer seeks for the cause of a star's variation in color, the biologist studies the life-history of a jelly-fish, the chemist prepares a thimbleful of some newly discovered compound, the mathematician speculates on the laws of a fourth dimension to space, while the mineralogist measures the angles of a microscopic crystal. These are the offerings on the altar of pure science; these are the theses of philosophers, and the life-works of scientists.

To the layman, the matter-of-fact man of the world, the study of pure science is a useless bit of mental recreation; an exercise in intellectual gymnastics which may strengthen and develop the mind, but which serves no other purpose. "*Cui Bono?*" he asks, with a shrug of the shoulders. What good is it all? For as humanity is more apt to reckon its honesty in terms of policy, so will it judge of knowledge by its usefulness. We have reached a period where utility is more and more in demand; a utility, moreover, which is reckoned in dollars and cents rather than in the more esthetic currency of beauty and truth. Things either have a money value or no value at all; ideas which cannot be patented are scarce worth the brain tissue used up in thinking them out. In an age when even the emotions are definitely assessed at certain money valuations, we should not be surprised to find that culture is rated below utility, and that the genius of the intellect is a servant in waiting to the God of Mammon. We do not rub the Lamp of Knowledge just to polish it up and keep it clean, but to summon the Slaves of Science that they may transmute for us the wealth of intellect into the wealth of the world.

The study of pure Science is essentially a study for culture. Leaving aside the consideration of any application of its results, it makes for increased intellectual powers by extending the intellectual vision; it elevates the type of knowledge and broadens the character of the individual. It differentiates from the universal "thought-stuff" another form of truth—a form, perhaps, which may exist as a piece of statuary which appeals to the artistic contemplation of the scientist, but which will never be animated with the energies of life. The question is narrowed down to one of appreciation and taste, and we must put to ourselves the query: Is the cultivation of pure science the essential element in the advancement of knowledge; or is it but a plaything and a hobby for the enthusiast, and does applied science become the absorbing purpose of knowledge and the ultimate foundation of truth? On the very threshold of this discussion we are struck with the disparity and wide separation of these two sides of scientific thought.

On the one hand we see pure science being carried out in the laboratories of universities and colleges, taking little or no thought of anything but itself. It labors faithfully and diligently onward to the working out of some engrossing idea—perhaps its end is the preparation of a hexachloride of molybdenum, or a determination of a velocity of a star through the shifting of lines in its spectrum; or possibly its goal is the tracing back of some English word to its derivation amidst its Aryan ancestors. But whatever the subject may be, the student of pure science will almost invariably lose sight of everything outside of that focus towards which all his lines of thought converge. He never stops to think for a moment what practical advantage to the world in general it will be whether Capella is moving away from the earth with a velocity of seventeen miles a second and not thirty-two, as some previous observer may have erroneously computed.

He may spend five years in preparing a single gram of the hexachloride of molybdenum, and after having established its composition and formula, and having used up all his product in so doing, he will experience a feeling of satisfaction at having so successfully completed a difficult problem in scientific research. After all, do not such things appear somewhat outside of the world's interest; are they really as much in touch with humanity as they should be? Can we altogether blame Swift for his little sarcasm about extracting sunbeams from cucumbers? It brings us around to the opinion that all science should be animated with a human motive; it should appeal to a wider interest than that of the mere student; it should be a living and organic force active within the life-history of thought itself. The truths of astronomy should appeal to more than a mere personal gratification of the star-gazer himself; every discovery of science should possess a universal significance before it becomes embodied in the general form of knowledge.

But on the other hand pure science, or science *par excellence*, is essentially a mode of intellectual culture, and as such cannot be regarded too highly as an end in itself. Whatever makes for the further development of the mind is more truly a factor in human progress than that which merely serves a utility in supplying the momentary demands of sense. The money value of a thing does not in any manner represent its final utility but merely serves to measure the present ratio between its demand and supply. Galvin spent years in patient study and research in observing the twitchings of the hind-legs of a frog; he did it purely for the interests of the science to which he had devoted his life, and no one paid him a cent for his trouble. But his seemingly trivial and ridiculous studies into the causes of the twitchings of the frog's legs proved to be the fount of inspiration from which flowed in a direct stream the discovery and knowledge of the electric current, and all the possibilities to which modern ingenuity has applied it. There is not a fact, however humble, but which by its understanding adds a dignity to human

knowledge; there is not a theory, however abstruse, but which by its confirmation and comprehension adds a new purpose to and widens the possibilities of human life. Our lives, in reality, are not made up so much of "things" as of "thoughts," and whenever science broadens the field of thought, she not only enlarges, but elevates the sphere of life. In estimating the utility of things we are inclined more to regard their individual practicability than their universal significance; a specific invention which earns its originator a material fortune is considered of more value in the opinion of most people than the broad law of nature to which that very invention owes its possibility and its conception. Men of science seldom patent the result of their research; they bend their energies towards the general expression of the truth of which they are in search; they care little, and in fact, know little, of the practical applications of that truth to the various needs of life. They find their greatest satisfaction and recompense in the consciousness of having advanced the general type of knowledge.

Perhaps we of the present time are inclined to depreciate the value of pure culture below that of mercantile utility, and give more attention to the transactions of commerce than to the speculations of science, literature, and art. The cry is often heard that we are rapidly going away from a civilization of pure culture to one of specialized utility; nor is this movement one peculiar to science alone, for we find it as an active factor in the fields of literature and art. Even the most conservative mind must admit the apparent fact that there is a strong force continually active in the direction of specialization, with the ultimate object in view of practical utility. The cause of its existence is found in the fact that human life is no longer commensurate with the infinite possibilities afforded for its activity; the ramifications of science have become so extended and numerous that should the individual desire to develop further, he must take up the burden of some specialized line and carry it forward in the rapid march of progress.

This is a period in which we are becoming steeped in education, flooded with knowledge. Our motto is becoming "It pays to know," and the particular knowledge which most pays to know appears to be of the scientific type. This is no doubt necessitated by the predominating influence science is exerting upon the numerous branches of industry and commerce. And our scientific education must be of a technical character in order to fulfil the exactions placed upon it. The development of technical sciences so closely allied to the arts is the direct result of the specializing of higher education so needful in the forming of acutely and minutely trained minds. This influence is becoming a potent factor in the educational problem of the times, giving knowledge a practical tendency and a body more in keeping with the flesh and blood of human needs. In making science assume a technical character there is an attempt to infuse the facts and energies of living industries into the rather inert and spiritual mass of general principles and theorems. What we know of as "pure science" has

little to do with the real problems of human life; these must be met and answered by the technical sciences, dealing as they do with practical applications of human knowledge.

You will pardon, I trust, these rather generalized reflections on the two aspects of chemical science, but I cannot help but feel that we are realizing a higher dignity for our science as a *profession* in contrast with its dignity as a purely academic form of scholarship and culture. Perhaps it was not so long ago that the chemical engineer was regarded somewhat as a pipe fitter and plumber, rather than as a real scientist. The chemist in England is still a drug clerk, and even to the layman in this country the chemist has been considered as a compounder of pills and hair tonics. The past two years I think, however, has seen a better appreciation by the layman and the press as to just what the chemist is and what his profession consists of and can accomplish. There is still that idea, however, prevailing that chemistry is a hodge-podge of mysterious secrets, the discovery of which is made by accidental and haphazard methods. The popular mind has evidently not yet progressed beyond the age of the alchemist. In things chemical the public has still the innocently receptive mind of a child; it will accept as gospel truth the most absurd and illogical statements of supposed discoveries. Some so-called chemist announces the remarkable discovery that by the addition of a few drops of a mysterious green liquid to water he creates a perfect substitute for gasoline for use in automobiles. The daily press devotes column after column to this truly remarkable process, and the public evidences the keenest and most serious interest. The thing could not be more absurd than if a physician announced that he had discovered that he could make new legs grow where those members had been amputated, by rubbing a decoction of hen's teeth on the parts affected. I hardly believe either the press or the public would take this latter announcement seriously and any editor would consider it too foolish to be printed. And yet how often have we been regaled at breakfast table with glaring head-lines announcing with all seriousness that Dr. So-and-So, a celebrated chemist (whom none of us had ever heard of before), has just discovered the *secret* of the German dyes.

Fortunately, however, I think the public and the press are becoming perceptibly educated to a saner idea of chemistry. We have all appreciated more or less the wide publicity given by the press to the recent meeting of our Society and we surely have not failed to notice the remarkably sensible and rational reports that were printed in our daily papers. We also could not but be impressed with the fact that the great throng of visitors to the Chemical Exposition was made up quite largely of laymen and the unscientific public, and they seemed interested and appreciative.

It is apparent, therefore, that chemistry is coming into closer contact with human life; it is becoming more and more a part of the every-day life of the world, and

as such is acquiring a breadth and a dignity which only a wide understanding can give it. And not only is the world at large being benefited by this wider understand-

ing, but chemistry itself, as a profession, is acquiring new forces and inspiration from this wider contact with human life.

Government Investigates Fertilizers

The annual report of the Chief of the Bureau of Soils, U. S. Department of Agriculture, announces that the fertilizer investigations of that bureau have been established as a separate administrative unit. The work of the division is divided along three lines which deal respectively with the three fertilizer ingredients—potash, nitrogen and phosphates.

Potash.—A plant will be erected on the southern Pacific coast to experiment on a commercial scale with the problem of extracting potash from kelp. This experimental plant is made possible by a special appropriation of \$175,000 for this purpose. The bureau also is co-operating with cement mills and blast furnaces to determine by analysis whether the potash now lost warrants the necessary expense to recover it. It is investigating the question of extracting potash from wool scourings and is making an effort to get in touch with companies in the country which are engaged in cleaning raw wool on a large scale. The bureau also has published a number of alunite determinations dealing with various methods of treating alunite for potash.

Nitrogen.—The bureau has equipped a laboratory at Arlington (Va.) Experiment Farm, with apparatus for testing the different methods proposed for fixing atmospheric nitrogen, and contracts have been let for much additional equipment to extend this work. This extension of the work has been delayed by the impossibility of securing immediate delivery of machinery.

In connection with the work on phosphates, an electrical furnace has been in operation working on the problem of volatilizing phosphoric acid and fixing nitrogen in one operation. Apparatus has also been installed for experimenting with the Ostwald process of oxidizing ammonia for the production of nitric acid. Both these projects are attended with technical difficulties and no important results can as yet be announced.

Investigations on city wastes have been continued and an apparatus and processes for rendering garbage and other similar wastes have been devised, which it is believed will prove superior to those now in use for this purpose. A full report on city wastes is now in course of preparation. Some work also has been done in determining the availability of various nitrogenous fertilizer materials when applied to the soil, and this work is being continued.

A study of the subject of ammonia from the by-product coke ovens has been made and published.

Phosphates.—At the Arlington laboratory an electric furnace has been installed and work on the volatilization of phosphoric acid from phosphate rock has been begun. A Cottrell precipitator was installed, and, while

minor adjustments remain to be made, the essential fact that phosphoric acid may be economically collected in this way has been demonstrated.

A process for producing sulphuric acid has been perfected and patented, which gives promise of being much more satisfactory than the process now in use.

The problem of producing concentrated fertilizers containing all three fertilizer ingredients or any two of them has been attacked from several directions, and methods have been worked out in the laboratory for producing ammonium-potassium-phosphate, potassium-phosphate and ammonium-phosphate by processes which are new and very promising. Patents on all these processes, for the benefit of the people of the United States, have either been secured or have been applied for.

GOVERNMENT POTASH PLANT.

In August, 1916, the Congress of the United States appropriated \$175,000 for the investigation of sources of potash within the United States. This appropriation was designed to make possible the continuation on a large scale of the work inaugurated and carried on by the Bureau of Soils of the United States Department of Agriculture. As a result of this work, and of the operations to date of the various commercial organizations engaged in the extraction of potash from kelp on the Pacific Coast, it appeared to the officials of the Department of Agriculture that the giant kelps of the Pacific Coast represented the largest and most immediately available source of potash in the country. Accordingly the Secretary of Agriculture has authorized the construction at some point on the coast of Southern California of a plant to be designed and operated to demonstrate on a commercial scale the various processes of extracting potash and by-products from kelp. This work will be carried on by the Bureau of Soils under the personal supervision of J. W. Turrentine. The bureau proposes to proceed at once with the execution of its plans.

BRITAIN PROHIBITS EXPORTS.

According to an official announcement by the British Government, the exportation of the following chemicals from that country will no longer be permitted: Bones in any form and bone ash; anthracite oil, mixtures and preparations containing the same; creosote and creosote oils; mixtures and preparations (except wood tar oil); green oil and mixtures and preparations containing green oil; muriate of potash; potassium sulphate; zinc oxide; guanous; manures and compound manures; organic phosphates; rock, namely, apatites, phosphate of lime and alumina; zinc dust.

Official Method of the American Leather Chemists' Association for the Analysis of Vegetable Materials Containing Tannin*

I. RAW AND SPENT MATERIALS.

(1) CAUTION: Proper care must be taken to prevent any change in the water content of raw materials during the sampling and preliminary operations. (See "General" under Sampling.)

(2) PREPARATION OF SAMPLE: The sample must be ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(a) The temperature used for drying samples of spent material for grinding must not exceed 60° C.

(b) Sample of raw material too wet to be ground may be dried before grinding as in (a). In this case a preliminary water determination must be made according to (IV) on the sample as received. If the portion of the sample taken for the water determination is in pieces too large to dry properly, it is permissible to reduce these to smaller size as rapidly and with as little loss of water as possible.

(3) WATER DETERMINATION: Ten grams of the ground material shall be dried in the manner and for the period specified for evaporation and drying in extract analysis (see IV).

(4) AMOUNT OF SAMPLE TO BE EXTRACTED: Such an amount of raw material shall be extracted as will give a solution containing as nearly as practicable 0.4 gram tannin to 100 cc. (not less than 0.375 or more than 0.425). Of spent materials such an amount shall be taken as will give a solution of as nearly as practicable the above concentration.

(5) EXTRACTION: Extraction shall be conducted in an apparatus consisting of a vessel in which water may be boiled and a container for the material to be extracted. The container shall be provided above with a condensation chamber so arranged that the water formed from the condensed steam will drip on the material to be extracted, and provided below with an arrangement of outlets such that the percolate may either be removed from the apparatus or be delivered to the boiling vessel. The boiling vessel must be so connected that it will deliver steam to the condensation chamber and that it may receive the percolate from the container. The condensation water from the condenser must be approximately the boiling temperature when it comes in contact with the material to be extracted.

The material of which the boiling flask is composed must be inert to the extractive solution. Suitable provision must be made for preventing any of the solid particles of the material from passing into the percolate.

(A) *Woods, Barks and Spent Materials*: Five hun-

dred cc. of the percolate shall be collected outside in approximately two hours and the extraction continued with 500 cc. for 14 hours longer by the process of continuous extraction with reflux condenser. The applied heat shall be such as to give condensation approximately 500 cc. in 1½ hours.

(B) *Materials Other Than Woods, Barks and Spent*: Digest the material in the extractor for one hour with water at room temperature and then extract by collecting two liters of percolate outside in approximately seven hours.

(6) ANALYSIS: The percolate shall be heated at 80° C., be cooled, made to the mark and analyzed according to the official method of extracts.

II. ANALYSIS OF EXTRACT.

(7) AMOUNT AND DILUTION FOR ANALYSIS: (A) *Fluid Extracts*: Fluid extracts shall be allowed to come to room temperature, be thoroughly mixed, and such quantity weighed for analysis as will give a solution containing as nearly as possible 0.4 gram tannin to 100 cc. (not less than 0.375 nor more than 0.425). Precautions must be taken to prevent loss of moisture during weighing. Dissolve the extract by washing it into a liter flask with 900 cc. of distilled water at 85° C.

Cooling: (a) The solutions prepared as above shall be cooled rapidly to 20° C. with water at a temperature of not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with at once, or

(b) The solution shall be allowed to stand over night, the temperature of the solution not being permitted to go below 20° C., be brought to 20° C. with water at not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with.

(B) *Solid and Powdered Extracts*: Such an amount of solid or powdered extract as will give a solution of the strength called for under liquid extracts shall be weighed in a beaker with proper precautions to prevent change of moisture. One hundred cc. of distilled water at 85° C. shall be added to the extract and the mixture placed on the water-bath, heated and stirred until a homogeneous solution is obtained. When dissolved, the solution shall immediately be washed into a liter flask with 800 cc. of distilled water at 85° C., be cooled, etc., as under (a) above.

NOTE: It is permissible to make up 2-liter instead of 1-liter solutions, dissolving by washing into flask with 1,800 cc. water at 85° C. in case of fluid extracts and 1,700 cc. water at 85° C. in case of solid or powdered extracts.

*From the November Journal of the American Leather Chemists' Association.

(8) TOTAL SOLIDS: Thoroughly mix the solutions; pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying." (See IV.)

(9) WATER: The water content is shown by the difference between 100 per cent and the total solids.

(10) SOLUBLE SOLIDS: S. & S. No. 590, or Munkell's No. 1 F, 15 cm. single, pleated, filter paper shall be used for the filtration.

The kaolin used shall answer the following test: 2 grams kaolin digested with 200 cc. of distilled water at 20° C. for 1 hour shall not give more than 1 mg. of soluble solids per 100 cc., and shall be neutral to phenolphthalein. To 1 gram kaolin in a beaker add sufficient solution to fill the paper, stir and pour on paper. Return filtrate to paper when approximately 25 cc. has collected, repeating operation for 1 hour, being careful to transfer all kaolin to the paper. At the end of the hour remove solution from filter paper, disturbing the kaolin as little as possible. Bring so much as needed of the original solution to exactly 20° C. as described under (7), refill the paper with this solution and begin to collect the filtrate for evaporating and drying as soon as it becomes clear. The paper must be kept full and the temperature of the solution on the filter must not fall below 20° C. nor rise above 25° C. during this part of the filtration. The temperature of the solution used for refilling the paper must be kept uniformly at 20° C. and the funnels and receiving vessels must be kept covered.

Pipette 100 cc. of clear filtrate into tared dish; evaporate and dry as under (8).

(11) INSOLUBLES: The insoluble content is shown by the difference between the total solids and the soluble solids, and represents the matters insoluble in a solution of the concentration used under the temperature conditions prescribed.

(12) NON-TANNINS: The hide powder used for the non-tannin determination shall be of woolly texture, well delimited, and shall require between 12 and 13 cc. of N/10 NaOH to neutralize 10 grams of the absolutely dry powder.

(a) Digest the hide powder with ten times its weight of distilled water till thoroughly soaked. Add 3 per cent of chrome alum, $(\text{Cr}_2\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, in 3 per cent solution calculated on the weight of the air-dry powder. Agitate frequently for several hours and let stand over night. Squeeze and wash by digesting with four successive portions of distilled water, each portion equal in amount to fifteen times the weight of the air-dry powder taken. Each digestion shall last for 15 minutes, and the hide powder shall be squeezed to approximately 75 per cent water after each digestion except the last, a press being used if necessary. The wet hide powder used for the analysis shall contain as nearly as possible 73 per cent. of water, not less than 71 per cent nor more than 74 per cent. Determine the moisture in the wet hide powder by drying approxi-

mately 20 grams. (See IV.) To such quantity of the wet hide as represents as closely as practicable 12½ grams (not less than 12.2 nor more than 12.8) of absolutely dry hide add 20 cc. of the original analysis solution and shake immediately for 10 minutes in some form of mechanical shaker. Squeeze immediately through linen, add 2 grams of kaolin (answering test described under (9)) to the detannized solution and filter through single folded filter (No. 1F Swedish recommended) of size sufficient to hold the entire filtrate, returning until clear. Pipette 100 cc. of filtrate into tared dish, evaporate and dry as in (8).

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Funnel and receiving vessels must be kept covered during filtration. Flasks graduated to deliver 200 cc. are recommended for measuring the analysis solution to be detannized.

(b) Digest the hide powder with the amount of water and add the amount of chrome alum in solution directed under (a).

Agitate in some form of mechanical shaker for 1 hour and proceed immediately with washing and subsequent operations as directed under (a).

NOTE: In order to limit the amount of dried hide powder used, determine the moisture in the air-dry powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing as nearly as possible 73 per cent. of water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

(13) TANNIN:

The tannin content is shown by the difference between the soluble solids and the corrected non-tannins, and represents the matters absorbable by hide under the conditions of the prescribed methods.

III. ANALYSIS OF LIQUORS.

(14) DILUTION:

Liquors shall be diluted for analysis with water at room temperature so as to give as nearly as possible 0.7 gram solids per 100 cc. of solution. Should a liquor be of such character as not to give a proper solution with water of room temperature it is permissible to dilute with water at 80° C. and cool rapidly as described under (7, A, a).

(15) TOTAL SOLIDS:

To be determined as in Extract Analysis.

(16) SOLUBLE SOLIDS:

To be determined as in Extract Analysis.

(17) INSOLUBLES:

Determined as in Extract Analysis.

(18) NON-TANNINS:

To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing as nearly as possible 73 per cent. water, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 cc.	Dry powder per 100 cc.
0.35—0.45 gram	9.0—11.0 grams
0.25—0.35 gram	6.5— 9.0 grams
0.15—0.25 gram	4.0— 6.5 grams
0.00—0.15 gram	0.0— 4.0 grams

Solutions to be shaken for non-tannins as in Extract Analysis and 100 cc. evaporated as in Extract Analysis.

IV. TEMPERATURE, EVAPORATION AND DRYING, DISHES.

(19) TEMPERATURE:

The temperature of the several portions of each solution pipetted for evaporating and drying, that is, the total solids, soluble solids and non-tannins must be identical at the time of pipetting.

(20) EVAPORATION:

All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer" at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(21) DISHES:

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2 $\frac{3}{4}$ inches diameter nor more than 3 inches in diameter.

V. DETERMINATION OF TOTAL ACIDITY OF LIQUORS.

(22) REAGENTS:

(a) One per cent. solution of gelatine neutral to hematine. The addition of 25 cc. of 95 per cent. alcohol per liter is recommended to prevent frothing. If the gelatine solution is alkaline, neutralize with tenth normal acetic acid and if acid neutralize with tenth normal sodium hydroxide.

(b) Hematine. A solution made by digesting hematine in cold neutral 95 per cent. alcohol in the proportion of $\frac{1}{2}$ gram of the former to 100 cc. of the latter.

(c) Acid washed kaolin free from soluble matters.

(d) Tenth normal sodium hydroxide.

DIRECTIONS:

To 25 cc. of liquor in a cylinder that can be stoppered, add 50 cc. of gelatine solution, dilute with water to 250 cc., add 15 grams of kaolin and shake vigorously. Allow to settle for at least 15 minutes, remove 30 cc. of the supernatant solution, dilute with 50 cc. of water and titrate with tenth normal soda, using hematine solution as the indicator. Each cc. tenth normal soda is equivalent to 0.2 per cent. acid as acetic.

VI. GENERAL.

(23) When materials containing sulphite-cellulose extract are analyzed, the fact that the material contains sulphite-cellulose extract shall be noted on the report.

(24) The test for the presence of sulphite cellulose in a liquor or extract shall be as follows: Five cc. of a solution of analytical strength shall be placed in a test tube, 0.5 cc. of aniline added and the whole well shaken; then 2 cc. of strong hydrochloric acid added and the mixture again shaken. If at least as much precipitate remains¹ as is obtained when a comparison solution prepared as below is similarly treated, the material shall be held to contain sulphite cellulose.

The comparison solution shall consist of sulphite cellulose in the proportion of one part total solids to 2,000 cc. of solution, and as much tanning material, similar to that being tested, but known to be free from sulphite-cellulose, as will make up the solution to analytical strength.

(25) On public analytical work by members of this Association the fact that the Official Method has been used shall be so stated.

OFFICIAL METHOD FOR SAMPLING TANNING MATERIALS.

GENERAL:

Extract, whether liquid or solid, and tanning materials in general all contain moisture. The amount of moisture varies with climatic conditions, but especially in liquid, and in most solid extracts becomes less as the extract is exposed to the air. As the value of any material shown by analysis is directly dependent upon the amount of moisture contained, and as an exposure of a comparatively few moments may alter appreciably the amount of moisture it is apparent that the sampling in all its details should be done as quickly as consistent with thoroughness and with great care to expose the material as little as possible to the air. The portions taken as samples should be placed at once in containers as nearly air tight as possible, and preferably of glass. Wood, cardboard, poorly glazed crockery, etc., are all porous and more or less absorbent and not suitable for retaining samples.

Liquid extract cannot be accurately sampled when it contains any frozen material. A sample of extract taken after live steam has been run into the extract has not the same concentration as the original extract. A sample of spent bark which has been standing where dust from fresh ground bark has sifted into it does not represent the degree of extraction of the spent bark. Samples of liquor which have been kept with no preservative in them for some time do not represent the condition of the liquor when sampled.

All extracts and crude tanning materials shall be sampled as nearly as possible at time of weighing, and for every 50,000 pounds, or less, sampled a sample shall be drawn.

(1) SOLID, POWDERED AND PASTY EXTRACTS:

The number of packages to be sampled out of a given lot shall be ascertained by taking a percentage of the total number of packages in the lot obtained in the following manner:—Divide the total number

¹Nepadal D gives the same reaction.

of packages by 100, multiply by 0.02 and subtract from 4.

$$\begin{aligned}\text{Thus } 4,700 \div 100 &= 47 \\ 47 \times 0.02 &= 0.94 \\ 4 - 0.94 &= 3.06 \text{ per cent.} \\ 4,700 \times 0.0306 &= 144 \text{ packages.}\end{aligned}$$

Provided that for lots of 200 packages and under 5 per cent. of the number of packages shall be sampled, and for lots of 10,000 packages and over 2 per cent. of the number of packages shall be sampled.

Whenever possible every Nth package shall be set aside for sampling while the extract is being moved. When this is not possible, the packages shall be selected from as uniformly distributed parts of the bulk as possible.

Samples of as nearly equal size as practicable shall be taken from each package and these samples shall represent as nearly as may be, proportionally the outer and inner portions of the extract. These sub-samples shall be placed in a clean, dry, closed container. When sampling is completed the whole composite sample shall be broken up until it will pass through a sieve of 1-inch mesh; it shall be reduced to the required bulk by successive mixings and quarterings. From this bulk duplicate samples of at least 6 ounces shall be drawn from opposite quarters by means of a small flat scoop (and not by selecting a handful here and there). The sample shall be enclosed in the smallest clean, dry glass receptacle, sealed and properly labeled.

NOTE:—Whenever possible the sample should be wrapped in paraffine paper and placed in the smallest straight-side glass receptacle; especially is this desirable during the warmer months of the year.

Sampling at place of manufacture shall be conducted by running a portion from the middle of each strike into a mold holding at least 2 pounds. These sub-samples shall be preserved with proper precautions against evaporation, and be sampled for analysis as above.

(2) LIQUID EXTRACTS IN BARRELS:

The number of barrels of extracts to be sampled out of any given lot shall be not less than 10 per cent. of the whole number of barrels for every 50,000 pounds or fraction thereof. The barrels to be sampled shall be rolled and shaken from end to end until the contents are homogeneous. Whenever this is not possible the heads of the barrels shall be removed and the contents stirred until homogeneous, a sample of equal size to be taken from each barrel. These sub-samples shall be put together in a suitable closed container and be thoroughly mixed. From this bulk duplicate samples of at least 4 ounces shall be drawn and preserved in clean, dry glass containers; sealed and labeled with such distinguishing marks as may be necessary.

(3) LIQUID EXTRACT IN BULK:

The extract shall be agitated with air, be plunged or be mixed by some other efficient means until homogeneous. Equal samples shall then be taken from differ-

ent parts of the bulk, be placed in a proper container, be thoroughly mixed and sampled as described in (2).

(4) LIQUID EXTRACT IN TANK CARS:

The following methods are permissible:

(a) The extract shall be unloaded into clean, dry containers and sampled according to (3); or,

(b) The extract shall be mixed until homogeneous, by plunging through the dome or other effective means, then numerous equal samples shall be taken from as widely scattered parts of the bulk as possible. These samples shall then be placed in a suitable container, be mixed and sampled as in (2).

NOTE:—As it is almost impossible to secure a homogeneous mixture of the extract in a tank car, this method should be used only when no other is possible. Or,

(c) The extract shall be sampled as follows while the car is being unloaded:—A quart sample shall be taken from the discharge three minutes after the extract has begun to run; another quart sample shall be taken three minutes before the extract has all run out, and three other quart samples shall be taken at equal intervals between these two. These five samples shall be transferred to a suitable container as soon as taken, be thoroughly mixed and sampled as in (2).

(5) CRUDE TANNING MATERIALS:

A. Shipments in bags, mats or other similar packages.

A number of packages shall be sampled representing 2 per cent. of the weight for every shipment of 50,000 pounds or fraction thereof, by taking representative portions from each package. These sub-samples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. Duplicate samples of not less than 5 pounds each shall be preserved in air-tight containers properly labeled.

B. Shipments in bulk, bark, wood, etc., in sticks.

Sticks shall be taken from at least ten uniformly distributed parts of the bulk, be sawed completely through and the sawdust thoroughly mixed and sampled as in "A."

C. Materials prepared for leaching.

Samples of equal size shall be taken at uniform intervals as the material enters the leach and be kept in a suitable container till sampling is completed. This bulk shall then be thoroughly mixed, be reduced by mixing and quartering, and duplicate samples for analysis of at least 2 pounds in size be preserved in air-tight containers, as in "A."

(6) SPENT MATERIALS FROM LEACHES:

Samples of spent material shall be taken from the top, middle and bottom, and in each case from the center and outer portions of the leach. These sub-samples shall be thoroughly mixed, be reduced in bulk by mixing and quartering, and duplicate samples of at least 1 quart in size be preserved for analysis.

(7) TANNING LIQUORS:

The liquor shall be mixed by plunging or other

effective means till homogeneous and then samples of at least 1 pint be taken for analysis. The addition of 0.03 per cent. of thymol or other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

When routine samples are taken from day to day and a composite sample analyzed, samples of equal size shall be taken from each vat after thorough mixing, be preserved in covered containers in as cool a place as possible, and be kept from fermentation by the addition of suitable anti-ferment, as above. This bulk shall be mixed till homogeneous and samples of not less than 1 pint each be preserved for analysis.

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the official method of sampling of The American Leather Chemists' Association."

OFFICIAL METHOD FOR ANALYSIS OF VEGETABLE TANNED LEATHER.

(1) PREPARATION OF SAMPLE:

The sample of leather for analysis shall be reduced to as fine a state of division as practicable, either by cutting or grinding.

(2) MOISTURE:

Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C.

(3) FATS:

Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent may be used for the determination of water-soluble material.

(4) ASH:

Incinerate 10 to 15 grams of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue. All the filtrate, evaporate to dryness and ignite.

(5) WATER-SOLUBLE MATERIAL:

Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for 3 hours. The total volume of solution to be 2 liters. Determine total solids and non-tannins according to the Official Method for extract analysis.

(6) GLUCOSE:

SOLUTIONS.

Copper Sulphate.—Dissolve 34,639 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 500 cc. Filter through asbestos.

Alkaline Tartrate Solution.—Dissolve 173 grams of Rochelle salt and 50 grams NaOH in water and dilute to 500 cc. Allow to stand 2 days and filter through asbestos.

Normal Lead Acetate Solution.—Prepare a saturated solution of normal lead acetate.

DETERMINATION.

Place 200 cc. of leather extract of analytical strength in a ½-liter flask, add 25 cc. of a saturated solution of normal lead acetate, shake frequently (5-10 minutes), and filter. (The funnels and beakers must be kept covered to prevent evaporation.) Add to the filtrate an excess of solid potassium oxalate. Mix frequently for 15 minutes and filter, returning the filtrate until clear. Pipette 150 cc. of this filtrate into a 600 cc. Erlenmeyer flask, add 5 cc. of concentrated HCl and boil under a reflux condenser for 2 hours. Cool, neutralize (place a small piece of litmus paper in the flask) with anhydrous sodium carbonate, transfer to a 200 cc. graduated flask and make to volume. Filter through a double filter. (The filtrate must be clear.) Determine the dextrose in the solution immediately.

Place 25 cc. of the copper solution and 25 cc. of the alkaline tartrate solution in a 400 cc. beaker. Add 50 cc. of the clarified and neutralized solution above mentioned and heat to boiling in *exactly* 4 minutes and boil for 2 minutes.¹ Filter immediately without diluting, *through asbestos*,² wash thoroughly with hot water, then with alcohol, and finally with ether; dry for ½ hour in water oven and weigh as cuprous oxide; determine the amount of dextrous by the use of Munson and Walker's table (Bull. 107: Rev. Bu. of Chem., p. 243) and report in percentage on leather.

¹The rate of heating of the Bunsen burner used should be regulated before sugar determinations are started. This is best done by adjusting the burner so as to bring 25 cc. copper soln. + 25 cc. alk. tartrate soln. + 50 cc. H₂O in a 400 cc. beaker to 100° C. in exactly four minutes.

²The finely divided, long-fibered asbestos to be used in the glucose determination should be digested with HNO₃, washed, then digested with NaOH and washed. When Gooch filters are prepared, they should be washed with boiling Fehling's solution, then with HNO₃. The mats thus prepared can be used for a long time.

Munson and Walker's Table.

(Bulletin 107, Revised, Bureau of Chemistry, page 243.)
(Expressed in milligrams.)

Copper. (cu.)	Dextrose. (d-glucose.)	Copper. (cu.)	Dextrose. (d-glucose.)	Copper. (cu.)	Dextrose. (d-glucose.)
8.9	4.0	44.4	21.3	79.9	38.9
9.8	4.5	45.3	21.7	80.8	39.3
10.7	4.9	46.2	22.2	81.7	39.8
11.5	5.3	47.1	22.6	82.6	40.2
12.4	5.7	48.0	23.0	83.5	40.6
13.3	6.2	48.9	23.5	84.4	41.1
14.2	6.6	49.7	23.9	85.3	41.5
15.1	7.0	50.6	24.3	86.2	42.0
16.0	7.5	51.5	24.8	87.1	42.4
16.9	7.9	52.4	25.2	87.9	42.9
17.8	8.3	53.3	25.6	88.8	43.3
18.7	8.7	54.2	26.1	89.7	43.8
19.5	9.2	55.1	26.5	90.6	44.2
20.4	9.6	56.0	27.0	91.5	44.7
21.3	10.0	56.8	27.4	92.4	45.1
22.2	10.5	57.7	27.8	93.3	45.5
23.1	10.9	58.6	28.3	94.2	46.0
24.0	11.3	59.5	28.7	95.0	46.4
24.9	11.8	60.4	29.2	95.9	46.9
25.8	12.2	61.3	29.6	96.8	47.3

Copper. (cu.)	Dextrose. (d-glucose.)	Copper. (cu.)	Dextrose. (d-glucose.)	Copper. (cu.)	Dextrose. (d-glucose.)	Copper. (cu.)	Dextrose. (d-glucose.)	Copper. (cu.)	Dextrose. (d-glucose.)	Copper. (cu.)	Dextrose. (d-glucose.)
26.6	12.6	62.2	30.0	97.7	47.8	239.8	122.5	279.8	144.7	319.8	167.5
27.5	13.1	63.1	30.5	98.6	48.2	240.7	122.9	280.7	145.2	320.7	168.0
28.4	13.5	64.0	30.9	99.5	48.7	241.6	123.4	281.6	145.7	321.6	168.5
29.3	13.9	64.8	31.4	100.4	49.1	242.5	123.9	282.5	146.2	322.4	169.0
30.2	14.3	65.7	31.8	101.3	49.6	243.4	124.4	283.4	146.7	323.3	169.6
31.1	14.8	66.6	32.2	102.2	50.0	244.3	124.9	284.2	147.2	324.2	170.1
32.0	15.2	67.5	32.7	103.0	50.5	245.2	125.4	285.1	147.7	325.1	170.6
32.9	15.6	68.4	33.1	103.9	50.9	246.1	125.9	286.0	148.2	326.0	171.1
33.8	16.1	69.3	33.6	104.8	51.4	246.9	126.4	286.9	148.7	326.9	171.6
34.6	16.5	70.2	34.0	105.7	51.8	247.8	126.9	287.8	149.2	327.8	172.1
35.5	16.9	71.1	34.4	106.6	52.3	248.7	127.3	288.7	149.7	328.7	172.7
36.4	17.4	71.9	34.9	107.5	52.7	249.6	127.8	289.6	150.2	329.5	173.2
37.3	17.8	72.8	35.3	108.4	53.2	250.5	128.3	290.5	150.7	330.4	173.7
38.2	18.2	73.7	35.8	109.3	53.6	251.4	128.8	291.4	151.2	331.3	174.2
39.1	18.7	74.6	36.2	110.1	54.1	252.3	129.3	292.2	151.7	332.2	174.7
40.0	19.1	75.5	36.7	111.0	54.5	253.2	129.8	293.1	152.2	333.1	175.3
40.9	19.6	76.4	37.1	111.9	55.0	254.0	130.3	294.0	152.7	334.0	175.8
41.7	20.0	77.3	37.5	112.8	55.4	254.9	130.8	294.9	153.2	334.9	176.3
42.6	20.4	78.2	38.0	113.7	55.9	255.8	131.3	295.8	153.7	335.8	176.8
43.5	20.9	79.1	38.4	114.6	56.3	256.7	131.8	296.7	154.2	336.7	177.3
115.5	56.8	155.5	77.4	195.4	98.4	257.6	132.3	297.6	154.7	337.5	177.9
116.4	57.2	156.3	77.8	196.3	98.9	258.5	132.7	298.5	155.2	338.4	178.4
117.3	57.7	157.2	78.3	197.2	99.4	259.4	133.2	299.3	155.8	339.3	178.9
118.1	58.1	158.1	78.8	198.1	99.9	260.3	133.7	300.2	156.3	340.2	179.4
119.0	58.6	159.0	79.2	199.0	100.3	261.2	134.2	301.1	156.8	341.1	180.0
119.9	59.0	159.9	79.7	199.9	100.8	262.0	134.7	302.0	157.3	342.0	180.5
120.8	59.5	160.8	80.1	200.7	101.3	262.9	135.2	302.9	157.8	342.9	181.0
121.7	60.0	161.7	80.6	201.6	101.8	263.8	135.7	303.8	158.3	343.8	181.5
122.6	60.4	162.6	81.1	202.5	102.2	264.7	136.2	304.7	158.8	344.6	182.0
123.5	60.9	163.4	81.5	203.4	102.7	265.6	136.7	305.6	159.3	345.5	182.6
124.4	61.3	164.3	82.0	204.3	103.2	266.5	137.2	306.5	159.8	346.4	183.1
125.2	61.8	165.2	82.5	205.2	103.7	267.4	137.7	307.3	160.3	347.3	183.6
126.1	62.2	166.1	82.9	206.1	104.1	268.3	138.2	308.2	160.8	348.2	184.1
127.0	62.7	167.0	83.4	207.0	104.6	269.1	138.7	309.1	161.4	349.1	184.7
127.9	63.1	167.9	83.9	207.9	105.1	270.0	139.2	310.0	161.9	350.0	185.2
128.8	63.6	168.8	84.3	208.7	105.6	270.9	139.7	310.9	162.4	350.9	185.7
129.7	64.0	169.7	84.8	209.6	106.0	271.8	140.2	311.8	162.9	351.8	186.2
130.6	64.5	170.5	85.3	210.5	106.5	272.7	140.7	312.7	163.4	352.6	186.8
131.5	65.0	171.4	85.7	211.4	107.0	273.6	141.2	313.6	163.9	353.5	187.3
132.4	65.4	172.3	86.2	212.3	107.5	274.5	141.7	314.4	164.4	354.4	187.8
133.2	65.9	173.2	86.7	213.2	108.0	355.3	188.4	382.0	204.4	408.6	220.7
134.1	66.3	174.1	87.1	214.1	108.4	356.2	188.9	382.8	204.9	409.5	221.3
135.0	66.8	175.0	87.6	215.0	108.9	357.1	189.4	383.7	205.5	410.4	221.8
135.9	67.2	175.9	88.1	215.8	109.4	358.0	189.9	384.6	206.0	411.3	222.4
136.8	67.7	176.8	88.5	216.7	109.9	358.9	190.5	385.5	206.5	412.2	222.9
137.7	68.2	177.7	89.0	217.6	110.4	359.7	191.0	386.4	207.1	413.0	223.5
138.6	68.6	178.5	89.5	218.5	110.8	360.6	191.5	387.3	207.6	413.9	224.0
139.5	69.1	179.4	89.9	219.4	111.3	361.5	192.1	388.2	208.2	414.8	224.6
140.3	69.5	180.3	90.4	220.3	111.8	362.4	192.6	389.1	208.7	415.7	225.1
141.2	70.0	181.2	90.9	221.2	112.3	363.3	193.1	390.0	209.2	416.6	225.7
142.1	70.4	182.1	91.4	222.1	112.8	364.2	193.7	390.8	209.8	417.5	226.2
143.0	70.9	183.0	91.8	223.0	113.2	365.1	194.2	391.7	210.3	418.4	226.8
143.9	71.4	183.9	92.3	223.8	113.7	366.0	194.7	392.6	210.9	419.3	227.4
144.8	71.8	184.8	92.8	224.7	114.2	366.9	195.2	393.5	211.4	420.2	227.9
145.7	72.3	185.6	93.2	225.6	114.7	367.7	195.8	394.4	212.0	421.0	228.5
146.6	72.8	186.5	93.7	226.5	115.2	368.6	196.3	395.3	212.5	421.9	229.0
147.5	73.2	187.4	94.2	227.4	115.7	369.5	196.8	396.2	213.1	422.8	229.6
148.3	73.7	188.3	94.6	228.3	116.1	370.4	197.4	397.1	213.6	423.7	230.1
149.2	74.1	189.2	95.1	229.2	116.6	371.3	197.9	397.9	214.1	424.6	230.7
150.1	74.6	190.1	95.6	230.1	117.1	372.2	198.4	398.8	214.7	425.5	231.3
151.0	75.1	191.0	96.1	231.0	117.6	373.1	199.0	399.7	215.2	426.4	231.8
151.9	75.5	191.9	96.5	231.8	118.1	374.0	199.5	400.6	215.8	427.3	232.4
152.8	86.0	192.8	97.5	233.6	118.6	374.8	200.1	401.5	216.3	428.1	232.9
153.7	76.9	194.5	98.0	234.5	119.0	375.7	200.6	402.4	216.9	429.0	233.5
377.5	201.1	403.3	217.4	429.9	234.1	376.6	201.1	403.3	217.4	429.9	234.1
377.5	201.7	404.2	218.0	430.8	234.6	377.5	201.7	404.2	218.0	430.8	234.6
378.4	202.2	405.1	218.5	431.7	235.2	378.4	202.2	405.1	218.5	431.7	235.2
379.3	202.8	405.9	219.1	432.6	235.7	379.3	202.8	405.9	219.1	432.6	235.7
380.2	203.3	406.8	219.6	433.5	236.3	380.2	203.3	406.8	219.6	433.5	236.3
381.1	203.8	407.7	220.2	434.4	236.9	381.1	203.8	407.7	220.2	434.4	236.9
435.3	237.4	435.3	237.4	435.3	237.4	435.3	237.4	435.3	237.4	435.3	237.4

(7) NITROGEN:

Gunning modification of the Kjeldahl Method, A. O. A. C. Bulletin, No. 107 (1907).

REAGENTS.

Standard Acid Solutions.—Hydrochloric or sulphuric acid, the absolute strength of which has been accurately determined. For ordinary work half-normal acid is recommended. For work in determining very small amounts of nitrogen, tenth-normal is recommended. In titrating mineral acid against hydroxide solution use cochineal as indicator.

Standard Alkali Solution.—The strength of this solution relative to the acid must be accurately determined; tenth-normal solution is recommended.

Sulphuric Acid.—The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

Sodium Hydroxide Solution.—A saturated solution of sodium hydroxide free from nitrates.

Potassium Sulphate.—This reagent should be pulverized before using.

Indicator.—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

DETERMINATION.

Place 0.7 gram leather in a digestion flask. Add 10 grams powdered potassium sulphate and from 15 to 25 cc. (ordinarily about 20 cc.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling point of the acid from 5 to 15 minutes or until frothing has ceased (a small piece of paraffine may be added to prevent extreme foaming).

Then raise the heat and boil briskly until the liquid has become quite clear and nearly colorless (the digestion should take from 4 to 5 hours).

After cooling, dilute with about 200 cc. of water. Next add 50 cc. soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distill until all ammonia has passed over into the standard acid. The first 150 cc. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1½ hours. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

PROVISIONAL METHOD FOR THE ANALYSIS OF ONE-BATH CHROME LIQUORS.

Chrome Determination.—Dilute a measured quantity of the liquor with water to a definite volume so

that the dilution contains from 0.15 to 0.25 per cent. of Cr_2O_3 . To 10 cc. of this dilution in a 300 cc. Erlenmeyer flask add about 50 cc. of water and about 2 grams of sodium peroxide. Boil gently 30 minutes, adding water if necessary to keep the volume from falling below about 15 c c. Cool, neutralize with strong HCl and add 5 cc. excess. Cool again. Add 10 cc. of a 10 per cent. solution of potassium iodide. After 1 minute run in from a burette 0.1 N sodium thiosulphate until the iodine color has nearly disappeared; then add a few cc. of starch solution (1 gram per liter) and titrate to the disappearance of the blue. One cc. of 0.1 N thiosulphate is equivalent to 0.002533 gram Cr_2O_3 .

Acid Determination.—Place 50 cc. of the above dilution in a 7-inch porcelain dish, add about 400 cc. of water and 1 cc. of a 5 per cent. solution of phenolphthalein and bring to a boil. While boiling, titrate with 0.5 N NaOH until the pink color persists after 1 minute boiling. One cc. 0.5 N NaOH is equivalent to 0.02002 gram SO_3 , 0.02452 gram H_2SO_4 , 0.01773 gram Cl or 0.01823 gram HCl .

Basicity.—The basicity is the ratio of basic radical to acid radical, found by dividing the percentage of Cr_2O_3 by the percentage of SO_3 or of Cl , carrying the quotient to two decimal places.

PROVISIONAL METHOD FOR THE ANALYSIS OF CHROME LEATHER.

Chrome Determination.—(a) Ash 3 grams of leather. Mix the ash well with 4 grams of a mixture of equal parts of sodium carbonate, potassium carbonate and powdered borax glass and fuse for 30 minutes. Dissolve the cooled fusion in hot water with enough HCl to make the solution acid. Filter. If there is any residue on the filter, ash it and treat the ash with 1 gram of the fusion mixture in the same manner as the original ash, adding the solution to the first. Make up to 500 cc. To 100 cc. of this solution in an Erlenmeyer flask, add 5 cc. HCl and determine Cr_2O_3 as above in the analysis of one-bath chrome liquors.

(b) If it is not desired to determine Fe or Al, the ash of 3 grams of leather may be transferred to an iron crucible, mixed with 3 grams of sodium peroxide and fused 10 minutes. Place cooled crucible in 300 cc. water in a casserole and boil 20 minutes. Wash into a 500 cc. flask, cool and make up to the mark. Filter through a dry filter. Place 100 cc. of filtrate in Erlenmeyer, neutralize with HCl , add 5 cc. excess and proceed as in (a).

PROVISIONAL METHOD FOR SULPHONATED OILS.

MOISTURE.

Weigh between 30 and 40 grams (depending on amount of water present) into a flask of 250 to 300 cc. and add 75 cc. water saturated xylol, prepared by heating a mixture of water and xylol with frequent shaking and subsequently removing the water in a

separatory funnel. Connect to a Liebig condenser and place flask in a bath of paraffine or a heavy lubricating oil. Distil moderately until the distillate comes clear. Collect distillate in a tube graduated to 1/10 cc. and wash condenser with a stream of xylol from a wash bottle. Place graduated tube in hot water and when the distillate is clear, cool. The percentage of moisture is obtained by dividing the volume of water in the distillate by the weight of oil taken.

NOTE:—For the graduated tube Eimer & Amend's No. 3812 is recommended.

ASH

Weigh any convenient quantity into a dish or crucible. Ignite gently, allowing the oil to burn and complete incineration until all carbon is consumed.

NON-SAPONIFIABLE.

Weigh approximately 10 grams of oil into an 8-ounce Erlenmeyer flask and add 5 cc. aqueous KOH solution (50 grams KOH in water and dilute to 100 cc.), 45 cc. ethyl alcohol and a few glass beads. Boil 1 hour with reflux condenser. Add 100 cc. water and cool. Transfer to separatory funnel and shake at least three times with petroleic ether (B. p. 40° to 75° C.) using 50 cc. each time. Wash ether layer at least three times with 50 cc. water containing 10 cc. ethyl alcohol. Use alcohol to break emulsion. Evaporate ether extract in tared vessel, cool and weigh.

NOTE:—If the contents of the flask bump violently during saponification add 25 cc. petroleic ether, and proceed.

COMBINED SO_3 .

(a) Weigh approximately 4 grams into an Erlenmeyer flask and boil for 40 minutes with 30 cc. HCl (1:5). Shake frequently. Cool, transfer to separatory funnel and shake out with petroleic ether. Draw off aqueous layer and wash etheral layer with water. Combine washings with main aqueous portion and the sulphuric acid determine as barium sulphate. From the amount thus found, the quantity as determined in (b) is subtracted and the difference calculated as SO_3 .

(b) Dissolve 4 grams in ether and shake out several times with 25 cc. concentrated brine free from sulphates. Combine the washings, dilute, filter and determine the sulphuric acid as barium sulphate.

TOTAL FATTY OIL.

The total fatty oil shall be the difference between 100 per cent. and the sum of moisture, ash and non-saponifiable.

NOTE:—The results obtained by these methods shall be reported only in one decimal place.

PROVISIONAL METHOD FOR ANALYSIS OF MOELLONS.

MOISTURE.

Weigh accurately 3 grams of the sample in a wide platinum dish, and heat with a low flame until the moisture is all driven off. This point can be deter-

mined by the appearance of smoke, and a slight crackling sound. Place the dish in a desiccator, cool and weigh.

ASH.

Ash the moellon remaining in the dish after the moisture determination in the usual manner, cool and weigh.

• UNSAPONIFIABLE.

Weigh accurately in a 300 cc. flask 5 grams of the moellon, add 2.5 grams caustic potash dissolved in a little water (or 5 cc. of a 50 per cent. KOH solution), and 25 cc. of 95 per cent. alcohol, boil with reflux condenser for 1 hour, shaking occasionally. Glass beads may be used to prevent bumping. Add 50 cc. hot water, cool, transfer to a separatory funnel, and extract three times, using 40 cc. petroleum ether for each extraction. A little alcohol may be added to break persistent emulsions. Wash the combined ether solutions three times with a mixture of 30 cc. of water and 10 cc. of alcohol, transfer to a tared dish, evaporate to dryness, cool and weigh. Excessive drying must be avoided.

OXIDIZED FATTY ACIDS.

Boil the soap solution remaining from the unsaponifiable determination until all the alcohol is expelled; then dissolve in hot water, transfer to a separatory funnel, rinse the beaker thoroughly into the funnel, bringing volume to approximately 300 cc., and immediately add a slight excess of concentrated HCl (about 25 per cent. more than sufficient to neutralize total alkali). Rotate the contents of the flask vigorously, cool and shake out with petroleum ether. Run off the aqueous layer, and pour off the ether layer, avoiding any loss of oxidized fatty acids. Wash these acids twice with small quantities of petroleum ether and hot water; dissolve in warm 95 per cent. alcohol, filter if necessary, transfer to a tared dish, and place in an ordinary evaporator and dryer for 16 hours; then cool and weigh. The entire operation should be conducted without delay.

FREE FATTY ACIDS.

Weigh out 1 gram moellon, dissolve in mixture of 20 cc. alcohol and 20 cc. sulphuric ether, which has been neutralized to phenolphthalein, and titrate with N/10 NaOH, using phenolphthalein as indicator. Test for mineral acids or alkalis (by adding methyl orange to the water emulsion of the moellon), and if present, make the necessary correction.

PROVISIONAL METHOD FOR ANALYSIS OF HARD GREASES.

TITER TEST.

Saponify 75 grams of fat in a metal dish with 60 cc. of 30 per cent. sodium hydroxide (36° Baumé) and 75 cc. of 95 per cent. by volume alcohol or 120 cc. of water. Boil to dryness with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of

boiling water and if alcohol has been used boil for 40 minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent. sulphuric acid (25° Baumé) to free fatty acids and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using hot water funnel, and dry 20 minutes at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 x 4 inches) and made of glass about 1 mm. in thickness. Place in a 16-ounce saltmouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8 x 6 inches), fit it with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermometer, graduated to 0.10° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for 30 seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

Place 3 cc. in a test-tube and add 15 cc. of alcohol (95 per cent. by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp. gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

UNSAPONIFIABLE.

Same as for Unsaponifiable in Moellons.

FREE FATTY ACIDS.

Same as for Free Fatty Acids in Moellons.

PROVISIONAL METHOD FOR THE ANALYSIS OF LACTIC ACID.

Free Sulphuric Acid.—Dissolve 50 grams of the sample in 200 cc. alcohol, which should be neutral, and of at least 95 per cent. strength. Heat to 60° C., cover and let stand over night in a warm place. Filter off precipitated material and wash with alcohol. Evaporate off the alcohol, make up residue to 250 cc. with water, add 5 cc. strong HCl, boil, add BaCl₂ and determine BaSO₄ in the usual way. Calculate to per cent. H₂SO₄ on the original sample.

Volatile Acid.—Weigh out 1 gram of sample, make up to about 50 cc. with water, titrate with 0.5 N NaOH. Calculate the result to lactic acid: (1 cc. 0.5 N NaOH = 0.045 gram lactic acid). On this basis make up a solution containing about 15 grams of acid per liter. Place 150 cc. of this dilution in a long-necked 300 cc. Kjeldahl flask, connected through a Kjeldahl bulb trap to a vertical spiral condenser, the

total height from the bottom of the flask to the top of the turn connecting with the condenser being between 20 and 24 inches. Distill over 125 cc. in from 47 to 53 minutes, counting from the time the first drop falls into the receiver, which should be a graduated cylinder. Add 125 cc. of water to the residue in the flask and repeat. Titrate both distillates with 0.1 N NaOH and phenolphthalein and calculate result to grams of acetic acid: 1 cc. 0.1 N NaOH = 0.006 gram acetic acid. From these figures for acid found in distillates find actual weight of volatile acid placed in boiling flask, by means of table, and calculate this result to percentage of volatile acid in the sample.

Table Showing the Relation of Amounts of Volatile Acid Found in Distillate Obtained Under Standard Conditions to the Amounts Actually Present in Distilling Flask, in Milligrams.

One Distillation.							
In distil- late.	In flask.	In distil- late.	In flask.	In distil- late.	In flask.	In distil- late.	In flask.
1	0.0	14	17.5	27	37.5	40	57.9
2	0.0	15	19.0	28	39.0	41	59.6
3	0.0	16	20.5	29	40.6	42	61.3
4	2.0	17	22.1	30	42.1	43	62.9
5	3.5	18	23.6	31	43.7	44	64.6
6	5.1	19	25.2	32	45.2	45	66.3
7	6.7	20	26.7	33	46.8	46	68.0
8	8.2	21	28.2	34	48.3	47	69.8
9	9.8	22	29.8	35	49.9	48	71.5
10	11.3	23	31.3	36	51.5	49	73.3
11	12.8	24	32.9	37	53.1	50	75.0
12	14.4	25	34.4	38	54.7	51	76.8
13	15.9	26	35.9	39	56.3	52	78.5

Two Distillations.							
In distil- late.	In flask.	In distil- late.	In flask.	In distil- late.	In flask.	In distil- late.	In flask.
5	0.0	22	19.2	39	38.9	56	58.6
6	1.0	23	20.4	40	40.0	57	59.8
7	2.0	24	21.5	41	41.1	58	61.1
8	3.0	25	22.7	42	42.3	59	62.3
9	4.0	26	23.9	43	43.4	60	63.5
10	5.0	27	25.0	44	44.6	61	64.7
11	6.2	28	26.2	45	45.7	62	65.9
12	7.4	29	27.3	46	46.8	63	67.2
13	8.6	30	28.5	47	48.0	64	68.4
14	9.8	31	29.7	48	49.2	65	69.6
15	11.0	32	30.8	49	50.3	66	70.8
16	12.1	33	32.0	50	51.5	67	72.0
17	13.4	34	33.1	51	52.7	68	73.3
18	14.5	35	34.3	52	53.9	69	74.5
19	15.7	36	35.4	53	55.0	70	75.7
20	16.9	37	36.6	54	56.2	71	76.9
21	18.1	38	37.7	55	57.4	72	78.1

Free Acid and Anhydride.—Titrate 50 cc. of the dilution made up for volatile acid, in the cold, with 0.5 N NaOH and phenolphthalein to first full pink. Call this figure "first titration." From it subtract a number of cc. of 0.5 N NaOH equivalent to the sum of volatile acid and free sulphuric acid present in the 50 cc. of dilution. (If the sample contains free oxalic or hydrochloric acid, the amount must be determined by appropriate methods, and further deduction made.) Calculate the remainder to lactic acid and express it as a percentage of the sample. This is the free lactic acid. After completing the first titration, add 4 cc. excess alkali, or in the case of concentrated acids 5 cc., and stand aside at room temperature (20°-25° C.), for 15 minutes. Then add 5 cc. 0.5 N H₂SO₄, boil, and titrate back with 0.5 N NaOH. The amount of alkali used by anhydride is now found by subtraction and calculated to lactic acid. Express this as per cent. of lactic acid equivalent to anhydride present in sample.

Some Experiences in Preparing Emulsion of Silver Iodide*

By JOSIAH C. PEACOCK and BERTHA L. DeG. PEACOCK

The so-called emulsion of silver iodide is a suspension of this compound in some suitable vehicle. It is probably well known to some and a total stranger to many others.

This subject has been treated by Mr. M. I. Wilbert in the American Journal of Pharmacy for February, 1906, and by Mr. J. K. Thum in the same journal for November, 1910, and November, 1915. Mr. Wilbert, where cited, mentions the availability of Irish moss, quince seed, salep and tragacanth as suspending media, and suggests a type-formula in which the silver iodide is first produced and then suspended in mucilage of Irish moss. Mr. Thum used the yolk of fresh eggs with ideal results, but brought about the formation of silver iodide in the presence of the yolk, instead of first forming the silver iodide and then suspending it as suggested in Mr. Wilbert's formula. Mr. Thum described mucilage of Irish moss as being, next to the egg yolk, the most efficient and satisfying agent. Mr. Thum also used solutions of gelatin ranging in strength from 0.1 to 0.5 per cent., which after frequent shaking during twenty-four to thirty-six hours brought the silver iodide into suspension; the solution containing 0.3 per cent. gelatin is mentioned as giving almost perfect results.

But it was our good fortune to be ignorant of this specific information, when about two years ago a physician gave an order for some five per cent. silver iodide emulsion to be ready in half an hour. We knew how to make silver iodide, but we had never been called upon to suspend it, and our inexperience in the matter gave us no little concern as we reflected on the possibility of turning out a satisfactory product.

We knew that an "emulsion" of silver iodide is used for photographic plates, and that gelatin is employed in this connection as the emulsifying agent, but not in a manner fit for our needs. Running over the list of eligibles in our minds, we felt that any one of several mucilages recalled might be as well suited as gelatin, and some one among us in the store remembered having heard of mucilage of Irish moss being used for the purpose. Coincidentally we were thinning some mucilage of tragacanth for pasting labels, and grasping the opportunity we took advantage of its readiness, and in less than the allotted time had an emulsion of fine appearance in the physician's hands. He remarked that he would need more within a few days, so we immediately prepared another portion with the mucilage of tragacanth, both to be ready and also to learn how well it would keep. For comparison, another lot was made with the aid of mucilage of Irish moss. Within a few days the emulsion produced with tragacanth had begun to darken somewhat and showed a tendency to settle a

coarse curdy precipitate, while that made with Irish moss retained its light yellow color and consistence for a much longer time. In fact, the color never perceptibly changed, although the silver iodide settled to some extent in the bottle.

Later, the physician reported that the lot which he received had retained its original appearance until used. But the use of Irish moss mucilage had, to our minds, improved the appearance and stability of the product so greatly that we decided to use it until an opportunity to look further into the matter of suitable suspending agents should come.

Accordingly, we examined mucilages made from sassafras pith, flaxseed, salep, elm, quince, dextrin, starch, and acacia, all of which are well known in use as emulsifying agents and emollient vehicles. We also repeated our experiments with tragacanth and Irish moss, and at the same time tried solutions of gelatin and egg albumen. Yolk of egg was not tried during this period, for it was looked upon as of itself too readily changeable.

After our experiments had been made and our conclusions drawn, we were apprised of the articles written by Mr. Wilbert and Mr. Thum. We have said it was our good fortune to be ignorant of the specific information given by these gentlemen; now the reason for so saying is not that we do not appreciate their work nor declare for their priority on all points in common, but had we known of their publications we most likely would not have made the many experiments performed for the purpose of this paper, and thereby would have been deprived of such knowledge as we have gained through personal experience with this subject. However, we present our experiences because they not only essentially conform to and thus confirm the statements of these gentlemen, but also mention some matters of interest not touched upon in their contributions.

Our object in making these experiments was to devise a plan to quickly produce a finely divided suspension of silver iodide and do so by introducing as little suspending material as possible.

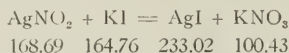
Silver iodide is affected by light, especially the actinic rays, when concentrated by a lens, but it is not so rapidly affected by diffused daylight or artificial light that it shows perceptible change in the time required to make an emulsion, and for that reason none of these processes need to be conducted in a dark room. Indeed, silver iodide has proven to be so permanent in these emulsions that we look upon the theory of its use as an antiseptic as somewhat of a conjecture of fact and fancy, to be settled by each practitioner for himself.

Unless otherwise specified our experiments were made on the basis of five per cent. silver iodide. Where a recognized formula for a mucilage existed, the pre-

*Paper read at the annual meeting of the Pennsylvania Pharmaceutical Association, June, 1916, and printed in the October American Journal of Pharmacy.

scribed strength and mode of preparation was followed, and the product used in the first trials with each individual mucilage.

The amounts of silver nitrate and potassium iodide needed to give the required quantity of silver iodide were calculated from the terms of the following well-known reaction:



the symbols of which, designated in molecular weights, as shown under them, respectively, indicate that 168.69 parts of silver nitrate require 164.76 parts of potassium iodide to produce 233.02 parts of silver iodide with the simultaneous formation of 100.43 parts of potassium nitrate.

In the course of this paper it will be pointed out that the specific gravity of mucilage of Irish moss, no matter how long macerated when prepared, is but negligibly more than water, therefore in our calculations for a five per cent. suspension we used 456 grains, or the weight of a fluidounce of water, as the 95 per cent. of vehicle per fluidounce, which calls for twenty-four grains of silver iodide as the five per cent. sought. By ratio, we find that 17.375 grains of silver nitrate are required to yield this silver iodide. A close scrutiny of the figures involved in the chemical reaction reveals the fact that just a little more of silver nitrate is required than of potassium iodide for accurate and complete interchange with each other.

Now the United States Pharmacopœa requires silver nitrate to be practically pure, so no allowance need be made on its part for impurities. But the same authority permits potassium iodide to contain one per cent. of impurities, consisting chiefly of chloride, carbonate and free hydrate, hence some allowance must be made for their most probable presence; and to commensurate for any deficiency of actual iodide, it has been suggested to use a slight increase over the theoretical amount of potassium iodide, and make the quantities of the two chemicals equal. This was invariably done by us, after we had learned by experience that as little as one-fortieth of a grain of unaffected silver nitrate which might remain in solution would very rapidly bring about discoloration of Irish moss mucilage.

There can be but little, if any, objection found to the presence of a minute excess of potassium iodide over that actually required, as it is imperative to completely precipitate the silver so that no soluble salt of it remains in solution, to act either as an undesirable application or as a factor to discolor the emulsion.

For quantities greater than one ounce of five per cent. emulsion, simply multiply 17.375 grains by the number of ounces required.

Silver iodide can, of course, be precipitated, washed, and then suspended in a mucilage, although it requires longer time to get it finely divided by agitation or stir-

ring, and for this reason the plan is not so well suited for hurried calls.

The products of our numerous attempts with this plan were not nearly so uniformly satisfactory as when the silver and potassium salts were dissolved each in one or two fluidrachms of distilled water and each solution diluted with a mucilage to half an ounce before mixing to form the insoluble silver iodide. In other words, the smoothness of the suspension was almost always superior when the reaction was brought about in the presence of a suitable mucilage, and if there is any chemical activity in the preparation, or if it is used solely as a protective application, it must be granted that the more finely divided the silver iodide the greater its efficiency.

When the precipitated silver iodide is not washed before suspending it, the emulsion will, of course, contain the potassium nitrate produced in the reaction, as also any excess of potassium iodide and other soluble salts originally present in the potassium iodide.

The amount of potassium nitrate formed in the preparation of a five per cent. emulsion is 10.34 grains per fluidounce, which equals a 2.27 percentage strength, which is three to four times the strength of the usual physiological or normal salt solutions. When intended for use in the eye, it may be thought necessary to rid the emulsion of soluble salts, although this may not be necessary in all cases, especially when we recall that ten to fifteen grains of borax or other salts are not infrequent ingredients in a fluidounce of eye drops. As a genito-urinary application the presence of these potassium salts is probably of little moment.

But if, for any reason, the emulsion must be free from soluble salts, the silver iodide may be produced from the water solutions of the necessary substances, thoroughly washed with either hot or cold water by decantation, and then incorporated in the suspending medium. Mucilage of Irish moss will serve here either hot or cold. Experience demonstrates that silver iodide settles very rapidly in hot water, and the expectation here would be to see the same thing happen; on the contrary, however, the hot mucilage envelops the silver iodide and overcomes this tendency to settle. Or, as we have found to be thoroughly practical when mucilage of Irish moss was employed, the emulsion may first be prepared by precipitating the silver iodide in the presence of the mucilage and the product then subjected to dialysis, using the ordinary parchment powder papers of the store as the necessary septum.

The former plan, for some reason which we have been unable to discern, unless it be attributed to allotropic conditions of the silver iodide, does not always show as smooth suspensions as would be desired; while the process of dialysis has almost always shown an improvement in this appearance, and has proven a simple expedient in ridding the emulsion of all crystalline matter.

Should it be deemed necessary to sterilize the emul-

sion either with the salts present or removed, it will be found that the preparation made with Irish moss will withstand this process. A sample subjected to streaming steam for three successive periods of twenty minutes each showed no change except a tendency to thicken slightly on the top surface, and was readily restored by shaking.

When silver nitrate was added to the several mucilages examined some of them showed a tendency to gelatinize, but none of them showed any appreciable precipitate of chlorides, so none were disqualified for such a cause.

Mucilage of sassafras pith, U. S. P., two per cent., failed to suspend the silver iodide, as did also a ten per cent. strength of mucilage. Both products showed stringy coagulations and curds and upon standing and shaking did not improve in miscibility.

Mucilage of flaxseed, twenty per cent., did not serve the purpose nor did one of 100 per cent. strength. The silver iodide went down in veritable lumps which were difficult and sometimes impossible to shake through the liquid.

Mucilage of salep, N. F., one per cent., did not satisfactorily suspend either three or five per cent. of silver iodide, and failed to perceive it; while a five per cent. salep mucilage suspended three per cent. of silver iodide moderately well, but very soon showed a change in color.

Mucilage of elm, U. S. P., six per cent., was not a satisfactory suspending medium by any means; neither was a twenty per cent. strength. This mucilage behaved very much like mucilage of sassafras pith.

Mucilage of quince, N. F., Appendix, of two per cent. strength, and even one of double strength, did not suspend either three or five per cent. of silver iodide. The ten per cent. mucilage yielded variable results, since in some instances it failed outright and discolored, while in others it gave quite satisfactory effects; and one of the most presentable three per cent. emulsions obtained from any experiment we made was afforded by a twenty per cent. mucilage of quince after twelve hours, almost without shaking, although when first made it was a hopeless looking mess of feathery precipitate. We have never been able exactly to duplicate this particular result, which emphasizes the uncertainty of quince mucilage. In the weaker strengths, when the mixtures did not approximate suspension, discoloration was soon observed. When silver nitrate is added to quince mucilage it coagulates it to an almost jelly consistence which requires long stirring to render it sufficiently thin to enable one to proceed with the work. It will therefore be recognized that quince mucilage is very poorly adapted to the purpose.

Mucilage of dextrin, N. F., thirty-three and one-half per cent., suspended the silver iodide, but decomposition began to show almost immediately.

Mucilage of starch, B. P., was prepared by thoroughly cooking starch with boiling water in the proportion of twelve grains to the fluidounce. In this strength of

starch mucilage the silver iodide mixed, but quickly settled, leaving a perfectly clear supernatant liquid of about one-third to one-half of the volume. This preparation had the distinction of being the only one from which the emulsified part separated to leave a clear liquid. A mucilage of twenty-four grains to the fluidounce behaved similarly.

Starch showed but very little tendency to discolor, and seems to be suitable so far as appearance of emulsion is concerned, although on several occasions samples of it became mouldy and displayed a musty odor within a week.

Mucilage of acacia, made according to the U. S. P. formula of thirty-four per cent. with thirty-three per cent. of lime water, had a slight acid or nearly neutral reaction. An alkaline mucilage must, of course, be avoided. The slightly acid mucilage of acacia gave good results, as did also a mucilage of the same strength made without lime water and possessing a strong acid reaction to litmus.

Half strength and quarter strength mucilage of acacia also showed good effects. These mucilages contain so much more solids than Irish moss mucilage, however, that they cannot be recommended in its stead.

Mucilage of tragacanth, U. S. P., six per cent., made with or without glycerin, was entirely too viscid, but reduced to one-quarter strength with water it suspended the silver iodide quite satisfactorily, but upon standing for a week or more showed in some samples an inclination to granulate, although some products containing it stood for months without showing much change in color. It can well be considered fit for any emulsions intended for prompt use, although it cannot be prepared as quickly as mucilage of Irish moss and for this reason is not so desirable.

Solutions of gelatin were tested as emulsifying agents only to find that concentrated ones were impractical to use in the presence of silver nitrate because it coagulated the gelatin so intensely; and that solutions which are diluted sufficiently to permit the addition of silver nitrate have very little immediate suspending action on it. For these reasons gelatin was discarded.

Egg albumen in full strength was coagulated so firmly by silver nitrate that it was rejected. Diluted with an equal volume of water it could be put through the process, but the result was a very curdy precipitate and so far from being satisfactory as scarcely to deserve mention along with Irish moss, tragacanth, acacia and starch.

In our original experiments little attention was intended to be given suspending media of animal origin, for the reason that they would putrefy. But after reading Mr. Thum's notes on this subject we decided to repeat our tests with gelatin and egg albumen, and also to try yolk of egg. As reported by Mr. Thum, we also found yolk of egg to be a very efficient and prompt suspending material, but the emulsion began to show a change in color in less than a week.

Compared with the preparation from Irish moss, it cannot be considered in any way superior.

From the foregoing statements it will be observed that some of the mucilages which have been treated of satisfactorily suspend silver iodide but discolor so rapidly as to be impractical, while others among them did not suspend it at all, even when tried in much greater strength than the recognized formula for that particular mucilage.

We have now reached mucilage of Irish moss, N. F., three per cent. It is undoubtedly the best practical emulsifying agent of all examined for the purpose, as every trial and test of it has proven. Its dependability and stability will unquestionably gain for it the commendation of all who try it for this purpose.

But before proceeding to tell the results of the experiments with the mucilage and silver iodide, mention should be made of some of the properties of Irish moss itself which were observed during these experiments. When dried it loses but a trifle in weight, indicating an almost total absence of moisture in its make-up.

The sample we examined and used for these experiments showed a loss of approximately ten per cent. of weight through the washing required to remove all but a faint trace of chlorine; the chlorine so removed represented in terms of sodium chloride six per cent. of the original substance. The water-insoluble substances present in the sample of moss amounted to ten per cent., which indicated a total of eighty per cent. of available water-soluble matter for mucilage.

As hereinbefore stated, it is a remarkable fact that a fluidounce of mucilage of Irish moss made according to the N. F. directions weighs but two and a half to three grains more than a fluidounce of water, making the increase in specific gravity over water practically negligible in all calculations, as it affects but the third decimal place. This fact remains the same whether the mucilage is prepared with hot or cold water. A fluidounce of the mucilage was evaporated in a platinum crucible in order to check up this paradox; the residue weighed less than three grains.

Mucilage of Irish moss is practically neutral to litmus paper, for it shows but the faintest acidity, and a very minute amount of fixed alkali will render several ounces of the mucilage alkaline to litmus and phenolphthalein.

Mucilage prepared by macerating Irish moss in cold water serves in every respect as well as the mucilage prepared with hot water and allowed to cool.

A series of mucilages were made by maceration in cold water for periods of fifteen minutes, thirty minutes, one hour and three hours, respectively, with the result that a fluid ounce of the thirty minutes, one hour and three hour samples were on an average within a grain of each other in weight, while the fifteen minute sample was within half a grain of the weight of the thirty minute specimen, demonstrating that thirty minutes maceration with cold water will produce a satisfactory mucilage.

After a number of tests made with the mucilage prepared in strict accordance with the N. F. directions, we finally devised the following plan, basing it on the results of our experiments:

Rejecting brown and harsher portions of the moss, select a few well-bleached and finely curled pieces to obtain the weight required; place these in a graduate and wash with several changes of water; as the texture softens, spread the branches to insure thorough washing; six to eight changes of water within two to three minutes will be found to be sufficient to remove the adhering chlorides. By this time the moss begins to swell and display a gelatinous surface and a test of the washings made now will show but a faint indication of chlorides. There need be no fear of overdoing the washing and thus losing mucilage, for as has been pointed out there will be an abundance of mucilage left to saturate the water. The moss is now macerated in a fresh portion of cold water with frequent stirring for half an hour, then expressed through well-washed muslin used double thick to obtain a clean mucilage. For each fluidounce of five per cent emulsion to be made, 17.375 grains of silver nitrate are to be dissolved in one fluidrachm of water and this solution mixed with three fluidrachms of mucilage of Irish moss. The same amount of potassium iodide should be dissolved in one fluidrachm of water, and its solution diluted to four fluidrachms with mucilage. The two solutions are now to be mixed by stirring together in order to thoroughly break up any curds of the silver iodide and facilitate suspension. The product may now be transferred to suitable containers.

In carrying out this process, it will be noted that the addition of silver nitrate to mucilage of Irish moss shows but little opalescence; but the silver nitrate causes the mucilage to thicken almost to the point of gelatinization, although it can be stirred into a uniform consistence. On the other hand, the effect of the potassium iodide was to lessen the viscosity of the mucilage of Irish moss.

The entire quantities of the solutions may be mixed at once, or one may be gradually poured or dropped into the other with constant stirring; there appears to be but little difference in behavior, unless it be that, when the entireties are mixed, more time is required to shake or stir into a uniformity of appearance. It seems not to matter which solution is poured into the other, for although silver iodide will dissolve in concentrated solutions of potassium iodide, the solution here employed is entirely too weak even in the beginning and of course is becoming weaker and weaker as the reaction progresses. The emulsions prepared with mucilage of Irish moss present at the time of reaction have seldom, if ever, failed to be smooth and uniform. We have never had a sample prepared in this manner darken or display any decided change in color, but we have had several samples made by first precipitating the silver iodide, washing, and then suspending, begin to darken within a few days.

Emulsions made with Irish moss may be diluted with water or with moss mucilage to make weaker preparations. Dilutions made with water settle more rapidly than those made with mucilage—a natural inference. Suspensions in Irish moss never settled entirely clear, as did starch emulsions. When the precipitate does settle in moss mucilage it appears to be still enveloped by the viscosity of the vehicle and may be easily restored by shaking. A sample prepared last August demonstrates this condition very effectively. It is also possible to make a ten per cent emulsion with moss mucilage, a sample of which, prepared a few months ago, is here shown (at Association meeting).

Owing to the heavy nature of silver iodide, it is evident that no emulsion should be used without shaking. In all of our experiments flint glass vessels and containers were used, and found to be thoroughly practical, and prolonged contact with cork stoppers has not in the least affected any of the emulsions which were satisfactory when first made, circumstances which compel us to believe that when once formed and protected with mucilage, silver iodide is quite a stable substance; in fact a sample exposed to bright direct sunlight for two days darkened but little, while a specimen unmixed with mucilage of Irish moss had turned dark gray within an hour under the same influence.

Irish moss, it occurred to us to dialyze it as a means of removing the salts in solution, and as a septum we used ordinary parchment powder papers. It required about twenty-four hours and five or six changes of water to extract practically all of the soluble salts. The emulsion was improved in appearance and consistence, through the removal of the crystalline constituents. A comparison was made by allowing a few drops of the original emulsion to spontaneously evaporate upon a smooth glass surface, with the result that the salts in solution were left as a crystalline centre in the residue, while a like performance with an emulsion from which the salts had been dialyzed showed no such crystalline residue, but instead a surface and appearance almost as smooth as a photographic plate.

The potassium nitrate left in the emulsion prevents the mucilage from decomposing, at least so far as odor is evidence. A sample prepared in August, 1915, gives no indication through odor of any change, whereas mucilage of Irish moss alone will within a week to ten days become obnoxious. Likewise, an emulsion from which the salts had been dialyzed developed an odor of putrefaction within a couple of weeks.

While it is evident that emulsion of silver iodide prepared by the method outlined will keep indefinitely, still if there is but an occasional call for it, and no need of keeping it ready made, the plans here and elsewhere given furnish a quick and thoroughly practical method for its production. But no matter which vehicle is used the facility with which silver salts are reduced by certain agents must be remembered so that all utensils used will be scrupulously free from such disturbing

causes, for aside from these there is little chance of failure.

Upon comparing mucilage of Irish moss with the other available vehicles, its advantage over tragacanth will be seen to lie in the ease of preparation; while its preference over starch and acacia comes through it introducing so little substance into the preparation.

The advantages of mucilage of Irish moss may then be emphasized as follows:

It can be depended upon as an efficient suspending agent.

It is easily and quickly prepared.

It gives a permanent emulsion.

It supplies a sufficiently viscid medium though adding but a trifle of solid matter.

It is as inert as any other suitable substance.

It is inexpensive.

While yet concerned with this subject a few words will be said regarding the sulphur which is present in Irish moss. To one who had never incinerated a vegetable drug and found a mass of hepar sulphuris as the resulting ash, it was a revelation to encounter such when some unwashed Irish moss was subjected to a bright red heat. With a lower heat very little sulphide is formed, but raised to bright redness, one can see a phosphorescence as of free sulphur burning, although sulphur dioxide could not be detected by odor. The fused mass amounted to 21.25 per cent of the original weight. Chlorides were present, of course.

Sulphates, earthy phosphates, carbonates, iron, aluminum, and silica were other constituents encountered in the examination of this ash, but no complete analysis was attempted.

A second weighed portion of moss was washed until it began to gelatinize, then dried and ignited. The result showed ten per cent of ash, and contained abundant alkaline sulphides, and a little chlorides.

A third weighed portion was completely exhausted by repeated applications of boiling water, the residue was dried and weighed. This insoluble part represented ten per cent of the original substance. It was next incinerated and found to yield 2.5 per cent of ash, calculated on original moss. The ash from this treatment was snow-white; it contained neither chlorides nor sulphides, but consisted of silicious matter. It is worthy of remark that in whatever form the sulphur exists in Irish moss, it has arranged itself in a very accommodating manner, so far as our present use for the mucilage is concerned.

CHILE TO SELL NITRATE LANDS.

Opportunities for American capital are disclosed in the announcement by the Charge d'Affaires of Chile, Washington, D. C., of a sale of nitrate lands in that country containing approximately 31,000,000 metric quintals. The lands will be put up at public auction by the Chilean government on April 16,

The Protection of Food Supplies*

By J. S. McCLUNE,

The protection of the food supplies of a nation is so evidently a necessity that advancing arguments to prove it would be only knocking down a strawman, since there are no arguments against it. There is no need then of more than mentioning the value of protection, but there cannot be too much or too frequent discussion of the means of protection. Eternal vigilance is necessary, and, as in all things, to hold our own we must advance. Much has been accomplished, especially since the beginning of the century, when agitation for and passing of food laws became a subject of public interest. But the work being done can and will be extended and improved, and a consideration of the means of improvement is very evidently a proper one for health officials.

In considering means of protection the basis of thought appears to be "From what are we to protect food?" The answer is summarized by "From adulteration and contamination." These are used in the broad sense of each word, adulteration meaning not just the legal definition, but any means by which the food appears better than it is, whether by fraudulent or dangerous addition or subtraction of constituents, false descriptions or misbranding, or even omission of true description whereby the purchaser is deceived; and contamination meaning injurious infection, whether by impure sources, spoilage of the food, or exterior pollution such as dirt, flies, or handling. Or in more concise form, *adulterated food* may be considered that *chemically inferior*, and *contaminated*, that *bacterially dangerous*.

Adulteration, in the sense above of constituents and description of foods, is a matter to be determined by analysis or inspection of foods by those experienced in the work. It is largely a matter for the federal or state governments to handle, with the assistance of any health officials or citizens interested, since it is somewhat costly and cannot be done on a small scale. Protection against adulterations, and, in this, forms of contamination are also included, is the object of the federal and state laws known as the pure food laws. What is being done should be of interest and can be outlined briefly.

The national law is enforced by the U. S. Bureau of Chemistry, so well started by Dr. Harvey Wiley and now under the able direction of Dr. Alsberg. The law covers foods and drugs imported or shipped in interstate commerce. The import work is rather quietly done, but is extremely effective, since the bureau here has wide powers and with goods which are not judged suitable the labels are changed or the intended uses modified to satisfy the officials in charge, or else entry

to the United States is refused. The interstate shipments when found in violation of the law or rulings under the law bring on prosecution or seizure of the material or fines against the shipper. Suits are continually being tried in the federal courts and notices of judgment published, which are more feared than the fines, unfortunately rather small in amount, because of the loss of reputation suffered. In addition, manufacturers and packers of food consult with the Bureau to comply with its regulations or profit by its advice. This is the work under the Food and Drug Act of 1906. In addition, there is the elaborate inspection of packing houses and meats which comes under the Bureau of Animal Industry and is of such benefit through its inspection at the source.

In the State of Ohio there are sections of the General Code very similar to the National Act, and these are enforced in the same way, by warnings and prosecutions. The enforcement of these sections is carried out by the Dairy and Food Division of the State Board of Agriculture. The many suits against the sale of illegal food products show the activity of this division, and by the notoriety obtained serve not only as a preventative for the offenders, but as a warning and education to other dealers and manufacturers. The state law of necessity holds the dealer responsible. It is often impossible for the state to reach the manufacturer, and the law is not framed to punish a criminal, but to protect the public consumer. In addition to protection there is the even more important work of the inspectors in visiting places where food is handled or sold, dairies, groceries, factories, markets and restaurants, and giving advice or warning. For the inspection work and the collection of samples with subsequent prosecutions if illegal, the Division has twenty-two inspectors assigned as follows:

- 6 Drug and Narcotic.
- 2 Weights and Measures.
- 14 Food, divided as:
 - 1 Cannery.
 - 4 Dairy and
 - 9 Food.

Perhaps an idea of the adulterations found may be best given by some actual examples, and I shall mention a few personally encountered in five years' work in the analysis of foods for the Federal Government and the State of Ohio. In some instances the talk of foods poisoned with preservatives and coal-tar dyes is an exaggeration, but there is serious and altogether too frequent adulteration of foods, and the need of government control may be demonstrated without departing in the least from facts. In the last two weeks one inspector has brought in 14 samples of milk served in various restaurants of one city in Ohio. Of these ten have been below the minimum legal requirement for fats—in fact, less than half the rather low re-

*From a paper presented at the Cedar Point Conference of Ohio Health Officers.

†Chemist, Division of Laboratories, Ohio State Board of Health.

quirement of 3 per cent fats. Of the fourteen, four were satisfactory, five skimmed, and five both watered and skimmed. Of course this does not mean that that percentage of the milk served in that city is adulterated, for the inspector selected his samples as suspicious, but it does show, I believe, that there is need of control. Samples of Hamburg steak are continually being brought to the laboratory which contains sulfites. This preserves the meat, but is both dangerous and illegal because it hides decomposition which may have taken place, and colors the meat red so that it appears better than it is. Suits are brought upon these samples and fines invariably imposed upon the dealers. Some caramels and chocolates tested last winter contained 14 to 17 per cent of paraffin—an inert substance, but not one that anyone would wish to feed to his child. In one government sample of peppermint extract, methyl alcohol was found. In the small amounts in which such a flavor is used it would probably not be injurious, but none wishes such a poison as that in his food. A chocolate paste was found to consist of 32 per cent water, 19 per cent dextrin, a starch of gummy consistency and 49 per cent hematite, or common iron oxid, which is used in our blast furnaces to make pig-iron. The manufacturer said this was a paint and not a food, but it was labeled on every can "Paste—Chocolate Style" and had been seized in the supply room of a bakery, so when the trial was held he did not appear with his rather thin story and upon the order of the court, the entire shipment was destroyed.

In the larger number of cases it is a question of fraud. Glucose, for instance, in spite of having been burdened with much suspicion, is, if properly prepared as it is now, not only harmless but very nutritious, but a dealer has no right to sell a jam with 50 per cent glucose as pure fruit jam—nor cottonseed oil for olive oil, nor oleomargarine for butter, nor any of the other many substitutions. The purchaser should be honestly and wholly informed as to what he is buying. One lawyer in a trial recently held in Ohio said that we state officials did not know the law nor our duties because we had not proved his client's goods injurious. But they were fraudulent and had been proved so, and to deceive purchasers in regard to their food is surely a punishable offense. Selling a solution of synthetic drugs colored with caramel for pure vanilla extract or a colored solution of dilute acetic acid for pure cider vinegar is a fraud and a crime equally with selling glass for a diamond or brass for gold. And in many instances such food frauds may bring about a loss in food values which makes the trickery a serious offense.

Examples could be extended almost indefinitely, but these few serve to show that adulteration is going on. However, much has been accomplished and manufacturers and dealers now risk fines and loss of reputation when they sell misbranded or adulterated articles of food. It may show a lack of the enthusiasm of the reformer, but I fear adulteration will always be with

us, since greed is such an element of human nature. But with increasing control and notoriety we may hope for continually lessened extensive and successful adulteration, and much has been and is being accomplished to keep impure foods off of the market.

Turning to what have been classed as contaminated foods, we find the cause of immediate danger and illnesses often fatal. While epidemics of diseases of the typhoid group, of septic sore throat and of diphtheria from infected milk supplies, and cases of poisoning from decomposing foods such as custards, fish, oysters, cheese and so on, are not frequent, they are, as we must admit, altogether too common. Such diseases and poisonings have been proved beyond any doubt to be due in many cases to food supplies, and there are other cases where some food is responsible, in all probability, though not so definitely proved. Ptomain poisoning—that is, the violent and dangerous illness caused by true ptomains formed in the decomposition of nitrogenous foods, is less frequent than reports indicate, since it is almost common practice to class all food poisoning as ptomain, whereas in fact the larger portion of it is caused by bacterial infection. But that is a matter of words which in turn are a matter of custom, and since our knowledge has not yet defined these groups very exactly, there is no use quibbling with words when we understand the use of ptomain poisoning as food poisoning. Whatever the term, the result is disagreeable, dangerous and often fatal, and the epidemics of disease from food supplies is even more serious.

The government agencies, federal and state, are fighting these dangers in every way possible with their present forces. The meat inspection referred to is wholly aimed at a maintenance of disease-free meat, and the food laws include in their definitions of adulterated foods, substances decomposed, putrid, or in any way unfit for consumption. The federal inspectors report on the sanitary features of factories visited, and the state inspectors are continually forcing the cleaning up of factories, canneries, dairies and restaurants with the authority given them by the Food sections of the Ohio Code.

It can readily be seen that here there is a different problem from that presented by the detection and punishment of chemical adulteration. It is of course of the highest value to discover the source of infection so as to remove it, but the object of this protective work is to prevent the formation of any source. Lives are involved and no measures should be omitted which will serve to keep the food supplies free from infection. Where food is handled in any way, cleanliness of materials, places, utensils and employes must be obtained, and strict quarantine of infectious diseases established. The efforts and co-operation of all health officials and food workers are absolutely necessary.

The services of local officials is of the greatest importance in such work. Without an enormous increase in forces, the federal and state departments cannot be

expected to watch all markets, groceries and restaurants, and each community must do much of this work itself. The larger cities have divisions in their health departments, or even Food Bureaus for such work, but the smaller communities must be protected by some official already established. Logically and legally, such official is the health officer. Section 4458 of the General Code is as follows:

"The board of health may appoint, define their duties and fix the compensation of such number of inspectors of dairies, slaughter-houses, shops, wagons, appliances, food and water supplies for animals, milk, meat, butter, cheese * * *, and such inspectors for such purposes may enter any house, vehicle, or yard. The board of health may appoint and authorize the health officer to perform the duties of such inspector."

The sections immediately following contain the powers and duties of such officials. Under the general powers conferred by Section 4404, the health officers may make rules, as you know, and Section 4413 further states:

"Orders and regulations not for the government of the board but intended for the general public, shall be adopted, advertised, recorded and certified as are ordinances of municipalities, and the record thereof shall be given, in all courts of the state, the same force and effect of such ordinances."

And these rules and regulations should be passed and adopted legally by advertising before epidemics or infection occur. When an offense is discovered, it is too late to begin to consider a rule against it—the ruling must be there so that action may be taken immediately. Without such legally adopted regulations, the health offices is powerless, for the general authority will finally rest upon personal opinion, which will not hold. But violation of definite rules does not depend upon opinion, but upon fact and results may be obtained. The law defines forms of adulteration, but protection from contamination must be established by the enforcement of measures for cleanliness and wholesomeness. These measures are not in the law, but become a part of it when provided by the adoption of rules and regulations."

The state Board of Health has published a pamphlet entitled "Orders and Regulations Recommended for Adoption by Village Health Officers." One portion is

devoted to rules for the protection of foods, and health officers are probably familiar with this. If not, it may be obtained from the State Board of Health. I shall not quote all of these sections, therefore, but the first, Number 42, is as follows:

"The health officer shall be the inspector of dairies, slaughter houses, * * * " and so on, following the wording of the Code given above. The regulations following treat of the permits for sale of milk or meat; testing of cows for tuberculosis; quarantine of infectious diseases at dairies; prohibition of the sale of adulterated milk or unwholesome food; of milk prepared under unsanitary conditions; same for meat; diseased or unwholesome food; provision for the covering of supplies exposed to flies, dust or dirt; and permits for selling ice.

These rules should be in force in every community. For flagrant violation of the dictates of food cleanliness they serve as the basis of punishment. But in most cases contamination is the result of carelessness rather than of viciousness. Education of the handlers of food is needed, and the adoption, publication and discussion of these rules will be the simplest and probably most effective means of starting education along these lines. The exposure of foods to dogs, dirt and dust of the streets, and flies and insects; the use of dirty utensils in preparing and serving food, the negligence of personal cleanliness in employees can often be remedied by simply having it called to the attention of those responsible. In other cases, warning may be necessary, in others perhaps prosecution, and here if it is not possible or advisable to undertake it alone the aid of the state and its inspectors may be secured by simply writing to the Dairy and Food Division, State Board of Agriculture, Columbus, Ohio. With the education of the dealers, and of the purchasers, who can exert an enormous influence, and by the activity of local officers and their co-operation with state officials, much can be done to lessen the dangers of infected or contaminated foods. As a move in this direction, it is intensely important that these rules and any others which may seem helpful should be adopted, and where adopted widely published and later absolutely enforced. With this further protection of food supplies, their purity may be increased or definitely established—surely one of the foundations for the building of public health.

Some Slow Volume Changes in Portland Cement*

By EDWARD D. CAMPBELL

Engineers have realized for many years that free lime and magnesia may cause dangerous expansion in Portland cement and have sought by specifications covering chemical composition and physical tests to eliminate trouble from these two sources. Free lime can be readily detected and its deleterious effect prevented by proper ageing of cement before use. Free magnesia, on the other hand, cannot be as readily detected and the expansion due to the presence of free magnesia does not manifest itself to any great extent in the length of time or under the conditions usually employed in testing Portland cement. It is for this latter reason that engineers who consider the safety of structures as the first requisite, usually specify a maximum allowable per cent of magnesia, low enough, so that under no conditions of ordinary practice and manufacture the amount of free magnesia could be large enough to produce serious results. If the total magnesia is kept under 3 per cent no trouble will arise from this cause under any circumstances.

On account of very extensive deposits of limestone too high in magnesia to permit its use in the manufacture of Portland cement if the allowable per cent of magnesia is kept down by specifications to 3 or 4 per cent, efforts have been made to produce from these magnesian limestones Portland cements which would satisfactorily pass all the physical tests to which these cements are usually subjected. Cements containing 7.5 or even 9 per cent magnesia have been prepared which have stood the ordinary physical tests and showed no abnormal expansion after intervals of 6 or even 9 mo. immersion in water. Anyone not familiar with the slow rate of hydration of magnesium oxide would naturally conclude that a cement which gave no abnormal expansion after 9 mo. immersion might be trusted in any work. It is because of this mistake that we are submitting some measurements which have been carried on in continuation of work described by the author in conjunction with Alfred H. White some ten years ago.

In this article, "Some Conditions Influencing Constancy of Volume in Portland Cements,"¹ the preparation and testing of a number of samples of cement of different degrees of basicity, some containing free lime, others free and combined magnesia, was described. The expansion measured by means of a special micrometer on bars 100 mm. in length was expressed in per cent, the measurements being made at increasing intervals of time. The time intervals selected were 7, 14, 21 and 28 days; 2, 3, 4, 6, 9, 12 and 18 mo.; and by intervals of 1 year each after the second year, the longest time recorded being 5 years from the time a given bar was made. The influence of chemical composition and ageing of the cement or clinker on the volume changes

was studied and the conclusions in part summarized as follows:

"Free lime in Portland cement will not only not be slaked during the mixing and setting of the cement but will not become completely hydrated even when the cement is immersed in water, until about 14 days have elapsed. The result of this gradual slaking is to produce abnormal expansion of the cement. Any evil effects due to the presence of free lime in cements kept under water will be manifested within 2 mo. In case free lime is present in cement used in structures above ground or where it is usually dry, the expansion due to hydration of the cement will be more gradual but several times greater in volume than when the material is under water. The expansion due to free lime slaking in the air may become so great after several months as to cause complete disintegration.

"The deleterious effects of free lime may be completely removed by ageing the ground cement or storing the clinker to weather until the pat will stand a perfect boiling test. Weathering the clinker for 3 mo. is usually sufficient. It is difficult to state the length of time necessary properly to age ground cement to eliminate free lime. It will not ordinarily be less than one month and may be much longer according to the conditions under which it is stored.

"Cement which passes a perfect boiling test may safely be assumed to contain no free lime. The expansion of a bar of neat cement containing no free lime when kept in cold water for 7 days is usually under 0.040 per cent, but occasionally it may go as high as 0.060 per cent. A cement with 2.8 per cent free lime showed an expansion of 0.220 per cent in the same period.

"The effect of magnesia, like that of lime, depends less upon its total amount than upon the form in which it exists. Combined magnesia like combined lime has no injurious effect in Portland cement. Magnesia combined with silica and alumina forms a hydraulic cement which is safe, but as compared with Portland cement is too weak to be of any commercial value. Free magnesia has no appreciable effect in cement used above ground where it is continuously dry. If the cement is wet for a part or whole of the time, the free magnesia will very slowly hydrate and cause expansion. Even where the cement is continuously immersed in water the expansion due to free magnesia is not appreciable until after 2 mo. and becomes distinctly evident only after a year. The hydration seems to be well under headway only at the end of the first year and expansion continues at an increasingly rapid rate for at least 5 yrs. and probably longer. Ageing does not seem to diminish the deleterious effect of free magnesia in cement. This is to be expected, since the rate of hydration of hard-burned magnesia in air is almost imperceptibly slow.

"The boiling test for 24 hrs. does not detect free magnesia as it does free lime. Cement containing as high as 4 per cent of free magnesia has passed a perfect boiling test, yet the last measurement of this cement at the end of 5 yrs. in cold water showed a total expansion of over 1 per cent, nearly half of which occurred during the fifth year after making.

"This slow hydration of free magnesia with its accompanying expansion seems to be the probable cause of the expansion, frequently accompanied by more or less complete disintegration, so often noted in sidewalks, occurring several years after the walk has been laid.

"One per cent, or less of free magnesia in cements kept under water causes little noticeable expansion even in neat cement, probably simply filling up the voids. Increased percentages of free magnesia cause cumulatively greater expansion until with 3 per cent of free magnesia the expansion is too great to be at all safe.

"In the manufacture of cement from raw materials containing magnesium carbonate, some portion of the magnesia will remain in the free state. This amount will increase with coarseness of raw materials, increasing percentage of lime and increasing percentage of magnesia. If the total magnesia does not exceed 3 per cent it is not likely that well-made cement will carry enough of this magnesia in the free form to cause injurious expansion under any conditions of service. If the percentage of total magnesia rises above 3 per cent there will be increasing probability

*From the Journal of Industrial and Engineering Chemistry, U. S. Am. Chem. Soc., 28 (1906), 1273-1303.

of enough magnesia remaining in the free form to cause injurious expansion."

Since the publication of the work summarized above, the experiments referred to therein have been continued, some of the periods being extended up to 13 and 14 years. As the purpose of the present paper is to call attention to the slow volume change, no measurements of expansion for a period of less than one year are given Table I, in which are shown the long-time measurements of expansion. If the short-time measure-

contains 0.53 per cent less silica and 0.67 per cent more calcium oxide than Expt. 79. The CaO ratio of Expt. 74 is 280.2 while that of Expt. 79 is 270.7 to 100 molecules of SiO_2 . In addition to the difference in basicity the raw material used in Expt. 74 was not quite as finely divided as that used in Expt. 79. Although in Expt. 79 by keeping the basic ratio low and having the material very finely ground, a cement was produced with a total magnesium oxide per cent of 7.2, and which would pass all the ordinary tests to which cements

TABLE I—EXPANSION OF BARS OF NEAT CEMENT IN WATER

All measurements represent percentage variation from original volume. All measurements represent expansion																	
EXPT. No.	MONTHS			YEARS												REMARKS	
	12	18	23	3	4	5	6	7	8	9	10	11	12	13	14		
74	A	0.370	0.423	0.447	0.499	0.550	0.582	0.592	0.611	0.625	0.665	0.678	0.688	0.688	0.710	0.720	Free CaO and free MgO
	D	0.102	0.121	0.164	...	0.245	0.285	0.307	0.344	0.360	0.372	0.378	0.385	0.391	0.415	...	Aged, Free MgO
75	A	0.355	0.383	0.390	0.407	0.370	0.432	0.424	0.407	...	...	...	...	...	...	...	Free CaO and free MgO
	D	0.130	0.136	0.152	...	0.177	0.188	0.185	0.204	...	...	...	...	...	...	...	Aged, Free MgO
77	A	0.130	0.163	0.158	0.170	0.180	0.190	0.180	0.166	0.188	0.193	0.189	...	...	...	...	Good cement used fresh
	D	0.033	0.037	0.043	...	0.052	0.056	0.051	0.060	0.063	0.061	0.053	...	...	...	...	After aging
78	A	0.390	0.414	0.412	0.421	0.441	0.451	0.441	0.428	0.457	0.460	0.458	...	...	...	...	Fresh, Free CaO
79	A	0.160	0.204	0.218	0.250	0.330	0.310	0.310	0.312	0.344	0.380	0.377	0.380	0.376	0.410	0.410	7.2% MgO, Fresh
	C	0.089	0.104	0.127	0.145	0.177	0.194	0.187	0.211	0.226	0.230	0.233	0.224	0.230	0.251	...	7.2% MgO, Aged
	E	0.095	0.117	0.140	0.180	0.212	0.222	0.247	0.262	0.278	0.279	0.285	0.285	0.306	...	...	7.2% MgO, Aged
80	A	0.032	0.057	0.062	0.082	0.100	0.102	0.091	0.072	0.093	0.107	0.102	...	...	...	...	All magnesia, Fresh
82	A	0.010	0.029	0.040	0.059	0.080	0.080	0.088	...	...	...	...	...	...	...	...	All magnesia, Aged
81	C	0.077	0.082	0.090	0.099	0.105	0.113	0.107	0.118	0.120	0.121	0.114	...	...	...	...	Same as 78, but aged
	B	0.049	0.051	0.059	0.071	0.070	0.078	0.072	0.081	0.085	0.085	0.073	...	...	...	...	Same as 78, but aged
	E	0.050	0.068	0.062	0.081	0.092	...	0.071	0.091	0.100	0.091	0.090	...	...	...	...	Same as 78, but aged
	G	0.089	0.103	0.101	0.115	0.121	0.115	0.104	...	0.125	0.122	0.122	...	...	...	...	Same as 78, but aged
83	A	0.100	0.112	0.116	0.132	0.139	0.144	0.140	0.149	0.150	0.155	0.150	0.145	0.143	0.134	...	Commercial cement, fresh
	B	0.095	0.106	0.117	0.134	0.144	0.146	0.146	0.165	0.169	0.170	0.163	0.168	0.160	0.173	...	Same + 1% free MgO
	C	0.113	0.133	0.150	0.170	0.190	0.203	0.200	0.225	0.223	0.232	0.232	0.240	0.232	0.242	...	Same + 2% free MgO
	D	0.127	0.151	0.168	0.197	0.253	0.382	0.525	0.862	1.002	1.072	1.069	1.072	1.067	1.097	...	Same + 3% free MgO
	E	0.158	0.172	0.223	0.290	0.562	1.010	1.390	1.965	2.185	2.280	2.280	2.285	2.284	2.298	...	Same + 4% free MgO
	F	0.093	0.106	0.110	0.119	0.129	0.130	0.122	0.140	0.131	0.140	0.139	0.137	0.133	0.141	...	Same + 1% combined MgO
	G	0.083	0.101	0.107	0.119	0.124	0.130	0.118	0.130	0.132	0.145	0.139	0.130	0.129	0.145	...	Same + 2% combined MgO
	H	0.090	0.101	0.106	0.118	0.130	0.138	0.125	0.148	0.147	0.150	0.149	0.140	0.143	0.160	...	Same + 3% combined MgO
	I	0.096	0.104	0.110	0.120	0.130	0.135	0.128	0.150	0.150	0.155	0.152	0.150	0.147	0.160	...	Same + 4% combined MgO
85	A	0.085	0.089	0.094	0.108	0.110	0.122	0.100	0.108	0.120	0.119	...	0.121	0.116	0.130	...	Same cement, aged
	C	0.067	0.074	0.079	0.091	0.100	0.104	0.086	0.099	0.110	0.108	0.095	0.101	0.092	0.110	...	Same cement, aged
	E	0.098	0.106	0.122	0.127	0.150	0.145	0.128	0.142	0.155	0.155	0.150	0.151	0.145	0.166	...	Same cement, aged + 1% free MgO
	G	0.107	0.124	0.135	0.154	0.165	0.185	0.175	0.195	0.215	0.216	0.213	0.214	0.206	0.229	...	Same cement, aged + 2% free MgO
	I	0.115	0.136	0.154	0.185	0.240	0.370	0.474	0.740	0.890	0.894	0.930	0.895	0.891	0.909	...	Same cement, aged + 3% free MgO
	K	0.141	0.175	0.199	0.282	0.615	0.944	1.311	5.222	1.575	1.581	...	1.580	1.578	1.601	...	Same cement, aged + 4% free MgO
	M	0.082	0.093	0.096	0.109	0.115	0.119	0.106	0.120	0.130	0.135	0.125	0.120	0.117	0.083	...	Same cement, aged + 1% combined MgO
	O	0.074	0.084	0.089	0.104	0.107	0.115	0.103	0.115	0.125	0.127	0.117	0.122	0.115	0.135	...	Same cement, aged + 2% combined MgO
	Q	0.070	0.080	0.087	0.108	0.099	0.109	0.101	0.118	0.130	0.131	0.125	0.128	0.120	0.169	...	Same cement, aged + 3% combined MgO
	S	0.052	0.062	0.069	0.081	0.084	0.095	0.089	0.109	0.119	0.124	0.115	0.122	0.112	0.139	...	Same cement, aged + 4% combined MgO

ments are desired, reference may be made to the above-mentioned paper. A study of the figures given in the accompanying table seems to sustain fully the conclusions drawn from the results published 10 years ago. The continued expansion due to free magnesia long after 5 years is very clearly brought out, as well as the fact that if magnesium oxide is in the combined form it will produce little or no volume change.

In view of the fact that efforts are being made to utilize, as a source of raw material for Portland cement, limestones too high in magnesia to enable the production of a cement low enough in this constituent to be safe under any conditions of manufacture, attention should be called to the results of the long-time measurements on Expts. 74 and 79. Both of these cements contain about 7 per cent total magnesia, but Expt. 74

would be subjected and which even after 13 or 14 yrs. immersion had not expanded to any extent which would probably be dangerous, yet a relatively slight increase in the basic ratio and coarseness of raw material has shown in Expt. 74 very nearly double the amount of expansion taking place after the first year, this increased expansion being due to the increased proportion of free magnesia. It is this liability of having a dangerous amount of free magnesia in cements made from raw materials much higher in magnesia than is usually considered permissible for the best quality that should make manufacturers very cautious about adopting high magnesia raw material and if they do employ such material they should realize that much greater care in manufacturing will be required to produce a reliable cement than if the purer raw material were used.

Ozokerite from the Thrall Oil Field*

By E. P. SCHLOCH

Ozokerite owes its use and value to the fact that it combines the great chemical inactivity or resistivity of paraffin with the physical properties of beeswax, namely, the property of being "doughy" or "kneadable." Its value is enhanced by the fact that its melting point is higher than that of paraffin or of beeswax.

Ozokerite and ceresine are used industrially in the manufacture of candles, in cable insulation, in shoe, stove and floor polishes. They are rather expensive—particularly at the present time because ozokerite is mined chiefly in Galicia. One New York firm, which buys large amounts of this material, stated that before the war Galician ceresine was worth 25 cents per lb., and that at present it was probably worth three times that amount. Ozokerite is found in the Caucasus, and in the Wasatch Mountains, Utah.

Some dark brown, waxy material, which is obtained together with crude petroleum at Thrall, Texas, has recently been analyzed in the Chemical Division of the Bureau of Economic Geology, and has been recognized as being *ozokerite* of an exceptionally good quality, as the following data show:

The crude material is soft, sticky, and of a dark brown color, with a sp. gr. of 0.875. It has a strong odor of crude petroleum. Heated to remove the latter, the crude material loses 14.72 per cent in weight up to 100° C., and 8.42 per cent more (or a total of 23.14 per cent) up to 180° C.

For refining, this heated material was treated with 18 per cent of its weight of concentrated sulfuric acid and the mixture heated at 180–200° C. until SO₂ ceased to be evolved. Then the mass was mixed with animal charcoal and "extracted" sawdust, the mixture heated for 20 min., then cooled and extracted with gasoline. On evaporating the gasoline, a material of the consistency of beeswax varying in color from orange-yellow to white was obtained. The white samples were practically free from the odor of petroleum, so that the color in the yellow samples was probably due to the presence of a trace of the original impurities. The amount of refined material thus obtained varied from 54 to 77 per cent of the weight of the crude material employed. Such refined ozokerite is technically known as *ceresine*.

Since the material might be either paraffin or ozokerite, a comparison with paraffin of the same consistency or hardness was made. The Thrall ozokerite is perfectly "doughy" and can be "kneaded," while paraffin is "flaky" and brittle.

Ceresine is distinguished from paraffin by means of its lesser solubility in carbon tetrachloride, carbon bisulfide, and chloroform:¹ 100 cc. portions of carbon tetra-

chloride dissolved 3.08 g. of Thrall ceresine, and 24.15 g. of "Texaco" paraffin, respectively.

The melting point of ozokerite² varies "from below 60° C. in the poorer grades to 68–75° C. in the normal quality, but may go as high as 84° C. (marble wax)." The Thrall ozokerite (unrefined) had a melting point of 79.5° C., while the refined material (The Thrall ceresine) melted at 75° C. The melting point of paraffin of the same consistency varies from 50 to 58° C., and that of "Texaco" paraffin was found to be 55° C. Thus melting point determinations indicate that the Thrall ozokerite is of fine quality.

The specific gravity² of paraffin (solidification point 44–58° C.) is 0.867–0.915 at 15° C., and of ceresine (solidification point 56–84° C.) it is between 0.912 and 0.943. The Thrall ceresine had a specific gravity of 0.926 to 0.928.

Various investigators have found that the indices of refraction of paraffins with melting points 50–58° C., range from 1.4220 to 1.4275 at 90° c., while the indices of refraction of pure ceresine range from 1.4212 to 1.4354, and even to 1.4415. The index of refraction of the Thrall ceresine was 1.4414 to 1.4420 at 90° C.

The purity of ceresine (particularly the absence of paraffin in it) is established by "fractional" dissolution and precipitation which, with a mixture of ceresine and paraffin, yields consecutive precipitates and a non-precipitable residue containing different proportions of ceresine to paraffin. This variation in the proportions of ceresine to paraffin can be ascertained by taking the indices of refraction of the consecutive precipitates and of the non-precipitable residue. With a pure ceresine, the indices of refraction of all the different precipitates should be well above the index of refraction for paraffin. On dissolution in chloroform, and precipitation with alcohol, the Thrall ceresine gave, on an average, the following indices of refraction:

First Precipitate	Second Precipitate	Residue
1.4400	1.4470	1.4420

This indicates that the Thrall ceresine is totally free from paraffin.

A sample of Galician ozokerite, secured in the open market for purposes of comparison, showed itself to be less "doughy" or kneadable than the Thrall ozokerite, and yielded a more flaky or brittle ceresine than the Thrall ceresine. Its melting point was low (55° C.); its index of refraction, 1.4420 at 90° C. This sample seems to be of a less desirable material than the Thrall ozokerite, but we do not know that it is a fair sample of Galician ozokerite.

These determinations show, beyond the question of a doubt, that the "Thrall" material is ozokerite, free from paraffin, and of a fine quality.

*From the Journal of Industrial and Engineering Chemistry. Published by permission of the Director of the Bureau of Economic Geology and Technology of the University of Texas.

¹Lewkowitsch's, "Analysis of Oils, Fats and Waxes."

²Holde-Mueller's "Examination of Hydrocarbon Oils."

³Holde-Mueller, p. 246.

BETTER SAMPLES FROM THE FERTILIZER FACTORY.*

By A. J. Lawrence.

A great many useless analyses are made through lack of co-operation between the laboratory and the factory and even where there is a strong desire on the part of the superintendent to have representative samples sent to the chemist, trouble often arises through incorrect methods of sampling.

In the fertilizer industry the methods of collecting samples vary to some extent in nearly every plant and we believe that by standardizing these methods, much trouble could be eliminated and more accurate and reliable information would result.

In receiving raw materials, some contracts specify as to the number of bags to be sampled. The large majority of sellers, however, leave the actual method of sampling to the sworn weigher. We have found considerable variance in the methods used by different weighers, many of whom do not realize the importance of their work and the trouble that may arise between buyer and seller owing to disagreement in analysis. An example of this is shown in a case in which there was considerable difference between the buyer's and the seller's chemists on a cargo of garbage tankage. The source of trouble lay in the fact that the sworn weigher, without consulting the chemist or sample-boy, had quartered the fluffy, dusty material during a very high wind, in which a large amount of the fine particles were blown away, and in leaving, told the sample-boy that he had gotten his sample and the remainder was in the barrel. The boy got his sample, not mentioning the incident, the results of which he did not realize.

Also, at times, where the samples are carefully mixed and quartered and the duplicates and triplicates agree excellently, still, lack of judgment in quartering on moist or dirty floors, or using brooms or shovels which are contaminated with foreign materials, will result in the analysis of the goods differing to some extent from that actually received.

A considerable loss of money can very easily result through using the "bought" analysis on a lot of goods, which analysis may be slightly different from that in the pile. In one instance, a low-grade tankage was sampled, the sworn weigher requiring the unloaders to take a handful from each cart and drop same into a burlap bag tacked to the side of the scales. A large tin bucket was put on the other side of the scale house, and the men were required carefully to take a cupful of sample from each cart and place same in the bucket. This experiment was tried because it was believed that in dropping the tankage into the bag, some of the fine ammoniated particles were lost by being blown away from the mouth of the same; also it was noticed that a considerable portion sifted through as each hand-

ful was thrown in. On several occasions the sample in the tin bucket showed a higher analysis, running from 26 to 90 cents per ton in valuation above that obtained on the sworn weigher's sample. The observance of these points would save considerable trouble later on should analysis be made in the piles and found to disagree with the "bought" test.

In batching stock brands which are to be shipped after being cured, we do not believe that enough stress is laid on the method of sampling. In the majority of plants, the usual plan is for the superintendent to run up several tons of a brand and either have a sample drawn from the mill or the carts as they dump into the pile, or have the sample-boy dig down a few inches into the pile at several places. In most instances, with careful sampling, fairly reliable results can be obtained in this way. However, from several experiments we find that quite often very bad analyses result from this method of sampling and cause numerous retests in the laboratory as well as new samples from the pile.

We believe that this trouble can be eliminated to a large extent by using a large prospecting auger such as is used in sampling soils and clays. This consists mainly of two blades arranged to cut a 6-in. hole and so bent as to pick up the material each time. Sufficient amount of handle can be attached to enable a pile of nearly any depth to be thoroughly sampled. In this way uniform sections can be bored into a pile in several places and duplicate samples invariably check, showing that if the materials are put into the mixture, a correct sample of same can be obtained.

The following tests were made on four brands of about 1000 tons each. Four samples were bored from each bin with the sampler as well as a sample being drawn from the mill during the run of the entire lot. The brands being figured to the exact analysis, the slight overrun is evidently due to shrinkage.

	"12-15-5" Brand	"10-8" Brand	"1-8-4" Brand	"2-8-10" Brand
	P ₂ O ₅ K ₂ O	P ₂ O ₅ K ₂ O	NH ₃ P ₂ O ₅ K ₂ O	NH ₃ P ₂ O ₅ K ₂ O
	12.55 4.96	10.05 7.91	1.15 8.05 4.00	2.18 8.15 10.20
	12.42 5.10	9.92 8.08	0.99 8.15 4.16	2.01 8.10 10.20
	12.48 5.12	9.96 8.10	1.03 8.15 4.04	2.11 8.17 10.01
	12.03 5.00	9.93 8.04	1.13 8.02 4.06	1.96 8.18 10.14
Av. (Bored)	12.52 5.04	9.97 8.03	.07 8.09 4.07	2.06 8.15 10.13
Mill sample } (Not Bored)	11.96 4.66	10.67 7.83	1.10 8.50 3.60	2.16 7.80 10.30

On these "mill" samples it would be necessary to change the formula which would result in incorrect analyses, whereas the bored samples show that the piles actually run about as figured. Bad analyses on bored samples can invariably be traced to faulty mixing in which either wrong amounts were weighed in or the actual materials fail to analyze as figured.

In sampling baggage shipments, we believe that much more reliable information can be obtained as to their analyses by the use of the double tube sampling trier which is inserted into a bag, closed, and withdrawn, giving an exact section of the material therein.

If methods of sampling could be as rigidly enforced in the factory as in the laboratory, we believe that more dependable information would result.

*From the Journal of Industrial and Engineering Chemistry. A paper presented at 53rd Meeting of the American Chemical Society, New York City, Sept. 25-30, 1916.

Heat Treatment of Brass in Neutral and Reducing Atmospheres*

By ALFRED H. WHITE and BERT A. STANDERLINE

Introduction.

When copper and zinc are melted together to form brass, and when brass billets or other articles are heated in annealing furnaces there is a material loss of metal. This loss is due in part to volatilization of the metal which is evolved as metallic vapor and is usually changed to oxide that passes away with the fume and is in part due to direct oxidation of the solid metal to form a scale which remains on the metal.

The volatilization of the metal is theoretically independent of the composition of the gases surrounding it, and if the reaction takes place in a closed vessel, and if sufficient time is allowed to attain equilibrium, is dependent only on the volume of the gases, the composition of the alloy and the temperature to which it is exposed. The relation of the temperature and the composition of the brass to the volatilization has been studied by Thorneycroft and Turner and is not discussed in this paper.

The volume of the gases surrounding the metal affects the volatilization materially for the amount of metallic vapor which a gas may hold is constant for a given temperature and pressure, and, therefore, in practice the greater the volume of gas and the more rapidly it is circulated over the metal the greater will be the volatilization in a given time. Theoretically the composition of the gas does not affect the volatilization of the metal, but this does not hold in practice for the metallic vapors become converted to oxides in an oxidizing atmosphere and equilibrium being thus destroyed, further amounts of metal volatilize. This is the case in the ordinary heat treatment of brass since both zinc and copper are readily changed to the oxides.

Copper-zinc alloys will suffer least loss in heat treatment at a given temperature if they are heated for as short a time in as small a volume of neutral gas as is possible. The small volume of gas may be attained if the metal is placed in a covered crucible as is done in the melting of brass or by the use of an externally fired muffle furnace. When, however, the door of the muffle must be opened frequently and the air space in the muffle is large, the circulation of the air within the muffle nullifies its advantage. An externally fired muffle also involves low fuel efficiency and a longer time to bring the metal to the desired temperature. There is also uneven heating in a muffle furnace, the material near the hot walls being necessarily heated more rapidly than in the center.

In a paper presented before this association last year as one of the results of your co-operation with the University of Michigan it was shown that it was possible to heat iron or steel to a temperature of 2,200°

F. for an hour without more than traces of oxidation, by exposing them directly to the gases formed by the combination of one volume of coal gas with about two volumes of air. The furnace used was a muffle heated both internally and externally. The mixture of gas with two volumes of air burned at the entrance to the muffle, the products of incomplete combustion passed through the muffle over the metal and out at the farther end where they mixed with more air, burned completely and passed back around the muffle. The theoretical temperature to be obtained from the combustion of one volume of coal gas and two volumes of air is 2,250° F., and with the aid of the secondary combustion outside of the muffle an actual temperature of 2,200° F. could readily be maintained within the muffle.

Under these circumstances about 27 per cent of the available heat was liberated in the primary combustion within the muffle and the remainder in the secondary combustion around the muffle. Of the products of combustion, steam and carbon dioxide, as well as any excess of oxygen act as oxidizing agents while hydrogen, carbon monoxide and any hydrocarbons act as reducing agents. With two volumes of air to one of unenriched coal gas the reducing agents have approximately 1.75 the volume of the oxidizing agents, while with 2.4 volumes of air to one of gas the reducing agents are still one and a half times as great as those which are oxidizing.

A gas of this neutral composition may be obtained from the partial combustion of natural gas, petroleum, coal gas or carburetted water gas. Producer gas as it comes directly from the producer may have also approximately this composition, although especial care would have to be given to the operation of the producer to obtain it, and it would be of variable composition. It would have to be used hot as it came from the producer, and only its sensible heat would be available for heating the material within the muffle, since if air were introduced for partial combustion it would raise the proportion of oxidizing gases. Walker has shown that it is practicable to use producer gas in annealing sterling silver, which contains 92.5 per cent of silver and 7.5 per cent of copper.

EXPERIMENTAL METHOD.

The general method was the same as that used formerly for the study of the heat treatment of steel. The furnace was a vertical muffle furnace consisting of a quartz tube with a Meker burner luted into the lower end. Both the gas and air entering this burner were metered, and as the mixture of air and gas rose within the tube and became heated it ignited so that the test piece hanging in the upper part of the muffle

*Presented at 25th annual meeting of Michigan Gas Association, Detroit, Sept. 21-22.

was surrounded only by the combustion gases. These gases of incomplete combustion passed out openings in the cap of the quartz tube into an annular space where they met secondary air sufficient for complete combustion and then passed down around the quartz tube and out of the furnace. A sketch of this furnace was given in the previous paper.

The heat treatment of brass does not involve such high temperature as the treatment of steel, but the volatilization of the zinc and the readier oxidation of both zinc and copper complicate the situation.

An unexpected complication in furnace construction was also introduced by this lower temperature, for a mixture of coal gas with even three volumes of air does not burn unless preheated. With higher muffle temperature used in the work on steel the gases were satisfactorily preheated as they progressed into the muffle. In the work with brass it was necessary to put in a checker work of refractory material over the gas inlet. This checker work became hot during the preliminary heating of the muffle with full oxidizing flame and maintained its heat during the subsequent operation with the reducing flame.

The experiments were conducted entirely on the laboratory scale and on three sets of materials—commercially pure copper, brass with 90 per cent of copper and 10 per cent of zinc, and brass with 70 per cent of copper and 30 of zinc. In ordinary commercial operations both the volatilization and the oxidation are dependent on the amount of surface of the piece rather than its weight. The material used in these tests was, therefore, always rolled into thin foil to give more surface, and in order to get this into a compact volume it was rolled into a loose spiral which was hung in the furnace with its axis parallel to the travel of the gases. The spiral was introduced into the preheated furnace and allowed to remain one hour. Special care was necessary in removing it from the furnace since the oxidation during the few moments required for cooling in the air would have been much greater than that involved in the furnace treatment of an hour. The spiral was chilled before removal from the furnace by lowering a short cast iron tube into the furnace and raising it so that the spiral dropped inside. The relatively heavy mass of the cold iron chilled the thin spiral so that it could be withdrawn without oxidation.

The changes in this foil due to the heating were determined by the change in weight and the visual appearance. Since the thickness of the foil was usually less than 0.003 inches, superficial alteration would have been delicately shown by the change in weight had it not been for the compensating action of the different changes. Volatilization of metal decreases its weight, while oxidation increases it. It is possible, therefore, to have a loss due to volatilization exactly compensated by an increase due to oxidation. The appearance of the surface indicates, however, when there has been material oxidation,

The gas used was in every case an unenriched coal gas of 600-615 B. t. u. per cubic foot. The composition of the products of incomplete combustion, their temperature and the thermal efficiency of the process were discussed in the former paper.

EFFECT OF HEATING COPPER AND BRASS IN A NEUTRAL ATMOSPHERE.

Commercial copper foil when heated in the gases formed by burning one volume of coal gas with three of air does not suffer an appreciable oxidation in an hour at a temperature as high as 1,178° F. The change in weight is negligible and the bright surface of the copper is scarcely tarnished. Details of the test are given in Table I on the opposite page. The behavior of copper at 1,500° F. is indicated by tests 24 and 25 of the alloy with 90 copper and 10 zinc, where with 2.5 volumes of air to one of gas the zinc was volatilized from the surface which was left a dull unoxidized copper color. A similar phenomenon was shown with the alloy having 70 copper and 30 zinc at high temperatures up to 1,798° F. as shown in tests 3, 4, 6, 10 and 11.

It is concluded that copper can be heated in this way to any temperature up to nearly its melting point without material scale formation.

The behavior of brass with 90 parts of copper and 10 of zinc is shown in tests 22 to 27. At 1,060 and 1,087° F. there was little effect due to an hour's heating in a mixture of 2.9 air to 1.0 of gas, the color being almost unchanged and the loss in weight trifling. At 1,224 and 1,242° with slightly more oxidizing conditions (3.2 volumes of air) the surface became gray and oxidized, but the weight was unchanged, the increase of weight due to formation of oxide being evidently compensated by the volatilization of the zinc. At 1,500-1,526° F. with a still more strongly reducing atmosphere (2.55 volumes of air) the metal became somewhat coated with lamp black, but when this was brushed off it was found that the surface was oxidized but had assumed a dull copper color due to volatilization of zinc from the surface. If the entire loss of weight can be laid to zinc, it indicates that about 40 per cent of the zinc was volatilized. This is apparently a large loss, but when it is considered that the foil was only 0.003 inches thick it is seen that this amount of zinc could have come from a surface layer only 0.0006 inches thick.

The brass with 70 per cent copper and 30 per cent zinc was given more attention than the others. This brass tarnished more readily than the others and it was difficult under any conditions to prevent it from showing a gray surface. At temperatures below 1250° F. (tests 1, 8, 9, 13, 14, 18, 19, 20, 21) with from 2.9 to 3.8 volumes of air to one of gas the change in weight was negligible and was sometimes a gain and sometimes a loss. At 1405° F. (test 12) with 3.02 volumes of air the loss in weight was about 0.9 per cent of the total weight or 2.7 per cent of the total

TABLE I.

Summary of Tests on Copper and Brass Heated for One Hour in an Atmosphere Formed by the Incomplete Combustion of Coal, Gas and Air.

No. of Sample	Temperature Max. °F	Temperature Min. °F	Ratio Air Gas	Area Test Piece sq. in.	Initial weight grams	Change in Weight Loss Grams	Change in Weight Gain Grams	Appearance After Test
A Commercial Copper.								
5	1162	932	2.93	8.32	1.5370		0.0007	Dark in Spots.
15	1139	1087	3.10	8.72	1.8089		0.0006	Bright.
16	1177	1123	3.00	8.50	2.1628		0.0013	Very slightly dull.
B Brass with 90 Copper and 10 Zinc.								
22	1060	1009	2.93	4.50	0.9032		0.0008	Dull copper color.
23	1087	1038	2.86	5.00	1.0078		0.0006	Dull copper color.
24	1526	1501	2.55	4.81	1.0778	0.0475		Dull copper color. Carbon deposited.
25	1504	1474	2.55	5.00	1.3067	0.0388		Dull copper color. Carbon deposited.
26	1224	1206	3.21	4.71	1.0270		0.0001	Gray.
27	1242	1215	3.18	5.39	1.2375	0.0000.	0.0000	Oxidized.
C Brass with 70 Copper and 30 Zinc.								
1	1197	1024	3.81	10.00	3.1569		0.0025	Gray.
3	1798	1724	1.33	11.52	3.5680	0.8370		Carbon deposited. Partially fused
4	1582	1461	1.93	9.96	3.3296	0.1142		Copper color.
6	1629	1508	2.33	7.38	2.5188	0.1273		Partly gray, partly copper color.
8	1114	1067	3.10	8.50	2.8698		0.0015	Fairly bright copper color.
9	1130	1062	3.19	6.84	2.3095		0.0007	Gray.
10	1526	1468	2.23	7.00	2.2048	0.2900		Grayish brass color.
11	1656	1603	2.23	7.86	2.1200	0.3377		Carbon deposited. Copper color.
12	1405	1249	3.02	7.38	2.3231	0.0215		Dull copper color.
13	1220	1189	2.91	8.11	2.2870	0.0003		Grayish brass color.
14	1141	1114	3.33	7.50	2.2216	0.0022		Grayish brass color.
18	1209	1188	3.81	6.09	2.2632	0.0004		Dull yellow brass color.
19	1215	1186	3.27	6.20	2.3222	0.0007		Grayish brass color.
20	1233	1143	3.28	6.00	2.1260		0.0001	Light gray brass color.
21	1162	1137	3.27	5.86	2.1200	0.0018		Light gray brass color.

zinc. At higher temperatures even with stronger reducing conditions the loss in weight was still greater.

In test 6 with 2.33 volumes of air to one of gas and a maximum temperature of 1628° F. the surface was a fairly bright copper color, showing that almost all of the zinc near the surface had been volatilized. The loss in weight was about 5 per cent of the total weight of the brass, corresponding to 15 per cent of the weight of the zinc.

At 1655°, as shown in test 11, the result was similar with a loss in weight of 16 per cent, corresponding to a removal of zinc from a layer only 0.0008 inches thick. The melting point of this brass is about 1760° F., and in test 3 this temperature was approached at the beginning of the test (1724°) and surpassed at the end of the test (1798°). The brass heated for an hour under these conditions in a strongly reducing atmosphere made by combining one volume of coal gas with 1.33 volumes of air became coated with carbon, but on brushing this off the metal was a dull copper color, showing occasional holes and fused globules of bright copper. The loss in weight was 23.4 per cent, corresponding to 78 per cent of the total zinc, or the amount of zinc coming from a layer 0.0012 inches thick. It is thus shown that brass can be heated, even up to its melting point for an hour in a stream of neutral gas with only trifling surface changes.

SUMMARY.

The method described a year ago for heating iron and steel in a neutral atmosphere has proved itself ad-

vantageous also for brass and copper. Copper is not oxidized when exposed directly to the products obtained from burning coal gas with an insufficient amount of air, the proportions of gas and air varying with the temperature to be reached. Up to 1200° F. three volumes of air to one of gas may be used, and still smaller proportions of air must be used for higher temperatures. The volatilization of the zinc from brass is primarily a function of the temperature, but can be reduced to a minimum by rapid heating and a neutral atmosphere which limits the loss to that due to temperature, and largely eliminates that due to oxidation.

This rapid heating in a neutral atmosphere can be readily obtained in a muffle within which coal gas is burned with an insufficient supply of air and around which these products of combustion are burned with additional air. The pieces placed within the muffle thus rapidly and evenly heated with a minimum loss of weight due to volatilization of the zinc. The loss of zinc after brass, with 70 copper and 30 zinc, was heated almost to its melting point for an hour amounted to an elimination of zinc from a layer only 0.0012 inches thick. With lower temperature even more favorable results were obtained.

The actual commercial value of this process can only be determined after tests on a large scale. There is every reason to believe that with the proper design of furnace it will be successful.

University of Michigan, August, 1916.

OCCUPATIONAL DISEASES IN THE CHEMICAL TRADES.

By Chas. Baskerville,* Professor of Chemistry, College of the City of New York.

An International Congress, dealing with the subject of industrial diseases, was held at Brussels in 1910. The first congress took place in 1906 in Milan, and since then an institution has been established there devoted to the study of diseases of occupation and to matters of industrial hygiene. Previously museums of safety had been established in Berlin (1904) and Vienna (1909).

The Brussels Congress was attended by over 600 delegates, and approximately 20 per cent. of the papers presented were by medical men of Great Britain, where the subject has received attention for a number of years, both by the Factory Department of the Home Office and by the Association of Certifying Factory Surgeons.

A Committee on Occupational Diseases in the Chemical Trades was appointed by the New York Section of the American Chemical Society in February, 1912. Some of the reasons for the existence of the committee appear in the statement of its objects, which were, specifically:

1. To hold itself ready to advise the Legislature of the State of New York in reference to matters appertaining to occupational diseases in the chemical trades;
2. To study various bills presented in the Legislature in an effort to avoid unwise technical legislation;
3. To superintend and inaugurate such investigations as might be decided upon which would look toward improvement of conditions of labor in the chemical trades.

Two members of that committee served the New York State Factory Investigating Commission and assisted in formulating the present laws having to do with inorganic chemicals, ventilation, and the regulation of the use of wood alcohol.

Subsequently the parent Society appointed the present committee, whose personnel has changed but little since its creation. The objects of this committee have been to extend the intent and purpose of the Sectional Committee in so far as legislation was concerned. It was and still is the hope of the committee to secure sane and uniform legislation in all the States.

Another purpose of the committee has been to learn of specific conditions in particular chemical trades which might call for improvement. To that end its members in the several parts of America represented have sought information, solicited and offered advice. It has co-operated with Boards of Health and private corporations. Its work, however, has not been systematic or in accordance with any well-defined plan, for the simple reason that no funds have been available to meet the expenses of investigation, adequate clerical

force for propaganda, etc. The work requires financial support to be properly organized.

Informally the committee has learned that some manufacturers are doing much toward the protection of their labor, while others are absolutely inconsiderate. The former are governed by altruistic motives, an appreciation of the efficiency of a healthy workman, and they are frequently supported by laws covering the employment of labor in factories. They are often handicapped, however, by unwillingness on the part of labor to utilize the precautionary facilities placed at hand.

The other group of manufacturers, fortunately relatively few in numbers, are selfishly inhuman in some instances and going their way lawlessly or more often in blind ignorance, for the untoward action of some chemicals is slow and insidious. In fact, one of the important questions in connection with industrial diseases is, "Is it possible to draw a distinction between maladies which are the result of certain occupations and accidents?" This is of great significance in connection with the "Workmen's Compensation Act" of England, and of the same importance in the relations between "Master and Servant" in this country. It is indeed difficult in many cases to ascertain whether a disease is the direct result of the nature of employment; but the justness of the principle of compensation for so-called industrial diseases is generally accepted, and the method of procedure by the aid of a schedule of diseases as adopted by the English law is regarded as a good example to follow. In the United States certain severe and clearly traceable diseases resulting from occupational causes have had recognition and active campaigns against such industrial maladies as plumbism and phosphorus poisoning have resulted in specified legislation.

Workmen's compensation laws have been enacted in about one-third of the States of the Union and there is hope that a Federal bill proposed may yet receive favorable action. The various State factory laws are, for the most part, however, concerned with minimizing fire-risks and obviating accidents to workmen engaged in purely mechanical operations.

Even though two excellent books on occupational diseases written in this country wholly or in part by some of the participants in this symposium have come from the press within the past two years, yet, as reverted to above, the action of some chemicals is insidious and not always known. It is of prime importance therefore that the introduction of any novel substance into industrial operations or the introduction of a novel procedure (electrolytic zinc at Anaconda, for example) should be studied to detect possible danger at an early stage so that due precautions may be taken. Usually trouble is recognized only after its results have become more or less pronounced, and hence we conclude that investigations on general industrial hazards should be carried on by the State, but only with co-operation of the manufacturers.

*Chairman of the Committee on Occupational Diseases in the Chemical Trades.

SOME SIMPLE CHEMICAL TESTS FOR LEATHER MAKERS.*

By A. Harvey.

It is now an established fact that a chemist is indispensable to a firm whose ambition it is to produce the best quality material at the lowest cost. From the point of view of the leather manufacturer, the word "adulterated" at once brings into his mind's eye a leather containing Epsom salts, or glucose; but of the hundred and one materials used in the making of the various classes of leather, the majority are open to adulteration. As adulteration—through the aid of science, I regret to say—has been brought to a fine art, the question of detection is made all the more difficult. Below, however, are appended a few simple tests which may be applied to several of the more common materials used, without the aid of a specially fixed laboratory or any expensive apparatus.

(1) *Lime*.—A good quicklime should slake well when mixed with water. If, on the addition of a little hydrochloric acid (spirits of salt) it effervesces, it points to a fair amount of chalk present, while if after this treatment with acid much is left undissolved, it would indicate an excessive quantity of sand or insoluble matter.

(2) *Linseed Meal* (Crushed Linseed).—Make a solution in hot water, and allow to cool. When cold, add a few drops of tincture of iodine. A blue color formed would show that the linseed had been adulterated. (The blue color really indicates the presence of starch, and pure linseed contains no starch.)

(3) *Dried Blood*.—If the amount of ash is determined, it should be between 4 and 5 per cent. It should be noted that the ash should be white. If of a brick-red color, the admixture of iron would be shown.

(4) *Gum Arabic*.—The likely adulterant is gum tragacanth. Dissolve some of the gum, after finely powdering, in the blue solution obtained by adding ammonia to a solution of bluestone (copper sulphate). If an appreciable amount is left undissolved, tragacanth is probably present.

(5) *Dyes*.—To determine whether a dye is just a simple one or an admixture, the following procedure should be adopted: Place a small portion of the dye on the end of a penknife, and blow it on to a piece of wet white blotting paper held about a foot away. The small particles will then adhere to the wet paper and dissolve in the water, showing its color. By this method one may show, for example, that a dye consists of a mixture of a blue and a red dye.

(6) *Cod Oil*.—This is likely to be adulterated with mineral oil. Boil up two or three drops of the oil with caustic soda which has been dissolved in methylated spirit. If after continued boiling a perceptible amount is left undissolved, this would indicate admixture with mineral oil.

This test is based upon the fact that, under the influence of caustic soda, cod oil is converted into soap, whereas mineral oils are not so changed.

(7) *Glucose*.—This substance may be adulterated, and if a small piece is burnt in a tin, only a very small amount of a white ash is left. Anything over a trace would indicate adulterants.

(8) *Salt*.—Impure salt may contain a small yet undesirable amount of iron. To test for this, make a solution of the salt in water, and add to it a few drops of potassium thiocyanate. In the presence of iron, a red color will develop. If this chemical is not at hand, add a few drops of potassium ferrocyanide (yellow prussiate), when a blue color will indicate iron.

(9) *Ammonium Chloride* ("Sal Ammoniac").—This should be of a pure white color, and perfectly soluble in cold water. If a small amount is heated in a tin lid over a gas flame it will be completely volatilized, no residue being left at all.

(10) *Caustic Soda*.—This substance, if left exposed to the air, will absorb carbon dioxide therefrom, and so gradually "carbonate." A rough test would be to dissolve a little of the sample in cold water, and then add a little hydrochloric of sulphuric acid (dilute). If gas bubbles are given off, this would indicate carbonates, which in a good sample should not be present.

(11) *Ferrous Sulphate* ("Green Vitriol").—A good sample should be of a uniform pale green color. In a moist atmosphere it is liable to undergo oxidation, in which case a brownish color will develop. To prevent this, the material should be kept in a cool dry place, for preference in large stone jars fitted with bungs.

(12) *Sodium Thiosulphate* ("Hypo").—It is quite unlikely that this chemical will be adulterated, but as in appearance it resembles soda, it may be confused with this if, say, the labels became detached from the receptacles in which they were kept. Add a little hydrochloric acid to a solution of the substance in water. If hypo, the solution will turn yellow (owing to the fine precipitate of sulphur) and an unpleasant smelling gas will be evolved (sulphur dioxide). If, on the other hand, the substance be soda, only bubbles of an odorless gas will be given off (carbon dioxide).

(13) *Flour*.—Alum is sometimes added to a bad quality flour in order to improve its appearance. To test for this substance, the following reagent has to be prepared: 10 cc. of 5 per cent alcoholic logwood solution mixed with 150 cc. of water, and 10 cc. of saturated ammonium carbonate solution. (This reagent should be mixed just before using.) Some of the flour to be tested is made into a paste with water, and then a few drops of the above solution added. Alum, if present, will be indicated by the formation of a blue color after the mixture has been allowed to stand for about two hours.

The percentage of ash also affords a good method of determining the quality of a flour. High-class flour yields 0.5 per cent of ash, whereas lower qualities will

*Journal of the American Leather Chemists' Association, in which it is reprinted from *Leather World*.

give from 0.5 up to 8 per cent, according to how much "bran" is present. Chalk, which some years ago was used as an adulterant, can be tested for by adding dilute hydrochloric acid to some flour paste, when an effervescence will take place if chalk is present.

(14) *Egg Yolk*.—It is difficult to suggest any simple tests for the purity of egg yolk, a chemical analysis being essential. The following tests, however, will detect the preservative present: Ignite some of the yolk to complete ash in a porcelain basin. If a large amount of a white ash is left, salt (sodium chloride) is the preserving agent. Now add to the ash a few drops of sulphuric acid, and then some methylated spirit. Warm the whole, and then ignite the spirit. In the presence of boric acid, a greenish tinge will appear around the edge of the flame.

(15) *Ammonia or ammonium hydrate* is a solution of pure ammonia gas in water, and at its greatest strength has a specific gravity of 0.880. A higher gravity than this would indicate either a weak liquor or the addition of water. If some of the solution is boiled to dryness in a dish, no residue should be left. Sulphates, chlorides, and other impurities are deposited by this treatment.

(16) *Borax*.—It is unlikely that this substance will appear adulterated, although soda has been stated to have been used for this purpose. This could be detected by treating some of the borax with some dilute hydrochloric acid, when, if soda is present, bubbles of gas will be evolved.

(17) *Mineral Acids*.—The two acids of this class used are hydrochloric and sulphuric, and to distinguish between these two, the following tests may be applied: Add to the acid (previously diluted with a little distilled water) a small quantity of silver nitrate solution. If a precipitate is formed, hydrochloric acid will be indicated. Using a fresh sample of the diluted acid, repeat the above experiment, using a solution of barium chloride in place of silver nitrate. A white precipitate will show sulphuric acid. By these tests, small amounts of impurities may be detected in either acid; for example, a very slight precipitate in the case of the first test will show a trace of chloride, etc. Iron may be detected in either acid by means of potassium sulphocyanide.

(18) *Shellac*.—The only impurity which can be demonstrated in a simple manner is any weighting material added, such as sand, etc., which may also be present in a dirty sample. Such substances will be left behind as insoluble residue when some of the material is dissolved in hot methylated spirit or hot ammonia solution. A good sample will dissolve completely in either of these two solvents.

(19) *Soda*.—*Washing soda or sodium carbonate* may contain iron and salt. Take some of the sample and dissolve it in some dilute sulphuric acid, or better still, some dilute nitric acid (aqua fortis). Divide the solution into two parts, and to one add a few drops of silver-nitrate solution, when a white curdy precipitate

will show the presence of salt. (If only a white cloudiness appears, a trace of salt is present.) To the other half of the solution add some potassium sulphocyanide, when a blood-red coloration will indicate iron.

(20) *Carbolic acid, or phenol*, which is sometimes used as an antiseptic, is liable to contain an undesirable amount of iron. The following method will apply: About half an ounce of the sample should be burnt to an ash in a porcelain dish. This operation should be performed in a place where the fumes evolved can be carried away—this is important. Then dissolve the ash in a few drops of strong nitric acid and dilute with a little water. The usual test for iron with potassium sulphocyanide may then be applied.

(21) *Sumac*.—The purity of this material, like all other tanning materials, can only be determined by an accurate chemical examination. Iron in a metallic form may sometimes be present in an undesirable amount. This may be tested for by running a strong magnet through a sample of the sumac previously spread out in a thin layer. The particles of iron will then adhere to the magnet, and may be removed and further examined if necessary.

(22) *Lactic Acid*.—If this acid has been adulterated with mineral matter, a large amount of residue will be left when some of the acid is boiled to dryness in a porcelain dish. To test for iron, the residue obtained above is dissolved in a little dilute nitric acid, diluted with a small quantity of water, and then a solution of potassium sulphocyanide added. If present, iron will give a deep red color.

NOTE.—This test also applies to acetic or formic acid.

(23) *Soaps*.—Soap, whether hard soap or soft soap, is very liable to adulteration with various admixtures. The sample should be cut into very small pieces, and a little of it boiled in absolute alcohol (or very good redistilled methylated spirit may be used). Only soap will be dissolved by this treatment. What is left will be alkaline carbonate, borate, silicate, together with any "filling material, such as starch, chalk, and, in very bad cases, even sawdust.

NOTE.—To detect iron in any material containing a large amount of organic matter, the following method may be applied: Burn the material to an ash in a porcelain (or better still a platinum) dish, and then heat the ash, when cool, with nitric acid. The addition of this acid is important, inasmuch as it converts all the iron present into the ferric condition, which is essential for the test. The resulting solution is diluted with a little water, and a little 10 per cent potassium sulphocyanide solution is added, when a red color shows the presence of iron.

Indicators.—By means of indicators one is able to tell whether a liquid has an acid or alkaline reaction. The following table gives the colors produced:

Indicator	If Acid	If Alkaline
Litmus	Red	Blue
Methyl Orange	Red	Yellow
Phenolphthalein	Colorless	Red

NOTES OF THE CHEMICAL AND ALLIED INDUSTRIES.

Alcohol.—John N. Lawler Co., of Alexandria, Va., has been incorporated with a capital stock of \$10,000 and proposes to engage in the manufacture of alcohol. John L. Lawler, Alexandria, Lewis Murdock and Jos. Edward of Washington, D. C., are interested.

Aluminum.—The Aluminum Ore Co., East St. Louis, Ill., has purchased a site and will expend perhaps \$700,000 for building equipment, etc. for a plant to be erected at Sollers Point, Md., for manufacture of anhydride of aluminum from bauxite ore. This company is a subsidiary of the Aluminum Company of America, Pittsburgh.

Cane Petroleum.—The Bayou Cane Petroleum Co., of Thibodaux, La., has been incorporated with a capital stock of \$50,000 and proposes to manufacture petroleum. Geo. F. Payne, Thibaux, and Henry Burgard, 2389 Berlin St., New Orleans, La., are interested.

Copper.—The Utah Copper Co., and the American Smelting & Refining Co., according to reports, will spend about \$10,000,000 in the next two years on improvements to their plants near Salt Lake City and at Tacoma, Wash.

Chemicals.—The Roessler & Hasslacher Chemical Co., Perth Amboy, N. J., has awarded a contract for the erection of the buildings for its plant at Lewis, W. Va. Total expenditure of about \$500,000 is proposed.

Chemicals.—Golding Chemical Co., St. Louis, Mo., is incorporated with a capital stock of \$50,000 and proposes to engage in the manufacture of chemicals. Geo. C. V. Fesler, J. M. Arndt, and H. E. Sprague are interested.

Chemicals.—The Gaylord Engineering & Construction Co., has been awarded a contract by the British Chemical Co., for erecting its plant at Trenton, Ont. The installation will include about 40 steel and concrete buildings, to cost about \$500,000.

Chemicals.—The Imperial Chemical Co., of Grand Rapids, Mich., incorporated recently, proposes to take over the Udell Chemical Co., whose plant has not been in operation for some time. Walter Ioor is president.

Chemicals.—The Sanol Chemical Co., of St. Louis, Mo., has been incorporated with a \$50,000 capital stock, and proposes to engage in the manufacture of chemicals. F. K. Wedemeyer, Wm. R. Gilbert and John H. Wedemeyer are interested.

Chemicals.—The Wisconsin Process Co., of Milwaukee, Wis., has been incorporated with a capital stock of \$10,000 and proposes to manufacture chemicals, etc. A. U. Stettin, E. W. Passmore and L. E. Fichaux are interested.

Chlorine.—The Warner Klipstein Chemical Co., 644 Greenwich St., New York City, has awarded the

contract to the Wm. L. Crow Construction Co., New York, for erecting two additional structures, 130 x 40 and 90 x 40 ft. to its plant at Charleston, W. Va. The company is now manufacturing chlorine and by-products from sodium chloride by the electrolytic process.

Cotton Seed Oil.—The Bain Mfg. Co., Pine Bluff, Ark., has been incorporated with a capital stock of \$30,000, and will equip a cotton-seed oil mill. D. B. Niven and A. J. Robinson are interested.

Drugs.—Sesame Pharmaceutical Corp., of Oklahoma City, Okla., has been incorporated with a capital stock of \$25,000 and proposes to engage in the manufacture of drugs. A. J. Cantrell and A. W. Dawson, Guymon, Okla., are interested.

Drugs.—Southern Pharmaceutical Co., Nashville, Tenn., has awarded a contract for a \$30,000 laboratory building to be erected on Main St. at Chattanooga, Tenn.

Dyes.—R. D. Gladney, of Sault, Miss., is understood to be organizing a company to manufacture fiber and dyes from cotton stalk.

Electro-Products.—The Shawinigan Electro-Products Co., of Baltimore, Md., proposes construction of an addition of another unit to its plant in Highlandtown, Md.

Fabrikoid.—Construction work is under way on a factory building to be erected at New Toronto, Ont., for the Dupont Fabrikoid Company of Toronto, manufacturers of leather goods; \$250,000 is proposed of which \$175,000 will be for machinery.

Ferro-Silicon.—The Guarantee Construction Co., 140 William St., New York City, has been awarded a contract by the Shawinigan Electro-Products Co., 1606 Public Service Bldg., Baltimore, for the construction of a fireproof building to cost about \$85,000. The equipment will cost about \$50,000 and will be of sufficient capacity to manufacture 75 tons daily at 50 per cent. ferro-silicon.

Graphite.—American Graphite Co., of Lineville, Ala., incorporated recently with a capital stock of \$40,000 proposes to establish a graphite plant at Lineville. S. C. Doby, Atlanta, Ga., and L. G. Brantly, Atlanta, are interested.

Hydrogen.—The Carbo Hydrogen Co., of Bayonne, N. J., has completed plans for the erection of a plant on Center St., in Cleveland, O.

Leather.—The Wilmington Leather Co., of Wilmington, Del., proposes construction of a six story factory, at Third and Greenhill Sts., Wilmington, to cost about \$60,000.

Lime.—Sampson Lime Mfg. Co., Wilmington, N. C., is incorporated with a capital stock of \$50,000. E. McN. Carr and L. C. Herring, interested.

Lime and Cement.—The Orangeville Lime & Cement Co. proposes the erection of a \$75,000 plant at Teeswater, Ont.

Minerals.—The Minerals Separation North American Co. has been incorporated in Maryland with a

capital stock of \$50,000,000 and proposes to engage in mining, engineering, buying and selling of all minerals, etc. Incorporators are Francis J. Carey, Calvert Bldg., Baltimore; Paul O. Carter and J. Bannister Hall, Jr.

Oil Refinery.—An expenditure of \$2,500,000 is proposed by the Melick Refining Co., for the construction of an oil refinery near Lexington, Ky. It is stated that work will be started next March.

Oil Refinery.—North American Oil & Refining Corp., Kansas City, Mo., proposes erection of an oil refinery in Sheffield Blue Valley District. The initial expenditure will be about \$100,000.

Oil Refinery.—The Paramount Oil & Refining Co., of Sapulpa, Okla., has been organized and proposes erection of an oil refinery. Richard Steinhorst, Okmulgee, Okla., is interested.

Oil Refinery.—The Standard Oil Co., of Kentucky. C. P. Collings, president, Louisville, Ky., proposes the expenditure of about \$1,000,000 for the erection of an oil refinery to manufacture a variety of oils including gasoline and have an annual capacity of 500,000 barrels.

Oil Refinery.—The Tulsa Gas-O Refining Co., of Tulsa, Okla., recently incorporated with a capital stock of \$600,000, proposes to operate an oil refinery. John B. Enfield, Tulsa, Okla., and J. L. Hughes, Enid, Okla., are interested.

Portland Cement.—The Universal Portland Cement Co., Chicago, Ill., has completed plans for a substantial enlargement of its plant at Buffington, Ind.

Potash.—A plant is under consideration for the manufacture of potash from seaweed of Sargasso Sea. W. S. Warner, 1001 Lafayette St., Tampa, Fla., is interested.

Pulp.—The Chicoutimi Pulp Co., of Chicoutimi, Que., of which J. E. A. Dubec is manager, proposes construction of addition to its plant, to increase the output from 80,000 to 130,000 tons of pulp per year.

Pulp.—The Colonial Pulp & Paper Mills, Ltd., of Quatsino Sound, Ont., proposes construction of a sulphite plant to have a daily capacity of 120 tons per year. The first unit will have a daily capacity of 60 tons, and will be completed in about a year.

Pulp.—The Beaver Board Timber Co., Ltd., Toronto, Ont., has been incorporated with a capital stock of \$50,000 and will engage in the manufacturing of pulp. John S. Duggan, 25 Harbord St., Toronto, is interested.

Pulp and Paper.—The Atlantic Paper & Pulp Co., of Port Wentworth, Ga., organized recently with a capital stock of \$1,500,000, proposes the construction of a plant to manufacture pulp and paper, to have a daily capacity of 50 tons. I. H. Fetty, Savannah, Ga., is president.

Pulp and Paper.—The Brompton Pulp & Paper Co., Ltd., Montreal, Que., has been incorporated with a capital stock of \$9,000,000. Errol Lanquedoc,

Ralph E. Allen, Pierce Charbonneau, are among the incorporators.

Soda Pulp.—The Varyan Rosin & Turpentine Co., of Brunswick, Ga., has had plans prepared by A. H. Ayerst, Engineer, Brunswick, Ga., for soda pulp mill of 50 tons daily capacity, as addition to its extract plant.

Sugar.—The Holly Sugar Co., Holly, Colo., is reported contemplating the establishment of a beet sugar mill at Plainview, Tex.

Tannery.—The Transylvania Tanning Co., proposes expenditure of about \$150,000 for the construction and equipment of a tannery at Brevard, N. C. Jos. S. Silverstein, Rosman, N. C., is president.

Turpentine and Rosin.—C. H. Turner & Co., Pensacola, Fla., have been awarded the contract for the building for a \$400,000 plant, to be erected at Pensacola for the Newport Turpentine & Rosin Co., of Milwaukee, Wis. This company recently increased the capital stock of \$100,000 to \$350,000.

LUMBER CENSUS TO INCLUDE PULPWOOD STATISTICS.

Figures showing the amount of wood used in the United States for making pulp will, it is announced, be obtained by the Forest Service in connection with its 1916 census of the lumber industry. Because of the increasing scarcity of pulpwood in some parts of the country the need for accurate figures showing the consumption of this class of material is realized by manufacturers and foresters alike and it is expected that such figures will be made a part of the yearly statistical work of the Forest Service. The pulp manufacturers will cooperate in the work, through their trade organization, the Newsprint Manufacturers' Association.

The data collected will comprise detailed information on the following:

Pulpwood consumption in cords by species, subdivided to show quantities of imported and domestic wood used. Comparative figures will be given for 1899, 1909, and 1914.

Number of mills by States; quantity of wood consumed; total cost; average cost per cord; amount of pulp produced.

Consumption of different kinds of pulpwood by States, subdivided to show amounts of domestic and imported spruce and poplar pulpwood.

Consumption of different species and different processes of manufacture.

Consumption by States, showing total amounts used, total cost and average cost per cord, according to condition of wood—rough, peeled, and rossed

The data to be obtained will, it is stated, be of considerable value to pulp manufacturers as well as to the Forest Service. Owing to the comparatively small number of pulp mills in the United States, it is thought it will be possible to issue a report on the work at an early date.

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